

APPLIED COLLOID CHEMISTRY

GENERAL THEORY

BY

WILDER D. BANCROFT

PROFESSOR OF PHYSICAL CHEMISTRY AT CORNELL UNIVERSITY

FIRST EDITION
SECOND IMPRESSION

McGRAW-HILL BOOK COMPANY, INC.
NEW YORK: 370 SEVENTH AVENUE
LONDON: 6 & 8 BOUVERIE ST., E. C. 4

1921

COPYRIGHT, 1921, BY THE
MCGRAW-HILL BOOK COMPANY, INC.

THE MAPLE PRESS YORK PA

PREFACE

The earlier books on colloid chemistry presented the subject empirically because no other method was then possible. While we do not now know much about gelatinous precipitates and jellies, the theory of the rest of the subject is in fairly good shape and consequently I have written this book deductively. While my point of view differs considerably from Freundlich's, it is a pleasure to acknowledge my debt to him for what he did in his admirable book.

This volume on general theory should be followed by at least one volume on each of the following subjects: silicate industries; paints and varnishes; plastics; fibers and dyeing; photochemistry and photography; petroleum industries; ore flotation and allied subjects; foods and beverages; soils and crops; biology and medicine. Allowing a minimum of three years to a volume, it seems very improbable that I shall write all of these single-handed. With the general theory of the subject once cleared up, there is no reason why the other volumes should not be written by people whose knowledge of the special subjects is much greater than my own.

I am indebted to Messrs. Bray, Briggs, Clowes, Holmes, Johnston and Lamb for reading the manuscript and for critical comments on it.

CORNELL UNIVERSITY,
November 1, 1920.

TABLE OF CONTENTS

	PAGE
INTRODUCTION	1
CHAPTER I	
ADSORPTION OF GAS OR VAPOR BY SOLID.	3
Adsorption of Gas or Vapor by Solid	3
The Adsorption Isotherm	29
Chemical Reactions	40
CHAPTER II	
ADSORPTION OF VAPOR BY LIQUID, AND OF LIQUID AND SOLID BY SOLID AND LIQUID	65
Adsorption of Vapor by Liquid	65
Adsorption of Liquid by Solid	67
Adsorption of Solid by Solid	78
Adsorption of Liquid by Liquid	81
Adsorption of Solid by Liquid	83
CHAPTER III	
ADSORPTION FROM SOLUTION	90
Adsorption from Solution by Solid	90
The Adsorption Isotherm	100
Abnormal Adsorption	106
Negative Adsorption	108
Reversibility of Equilibrium	110
Specificity of Adsorption	111
Adsorption of Several Solutes	113
Chemical Action	120
Adsorption from Solution by Liquid	126
CHAPTER IV	
SURFACE TENSION—BROWNIAN MOVEMENTS	129
Adsorption and Surface Tension	129
Brownian Movements	136
CHAPTER V	
COALESCENCE	146
Coalescence of Liquids	146
Coalescence of Solids	147
Types of Precipitates	161
Theory of Peptization	166

CONTENTS

CHAPTER VI

	PAGE
PREPARATION OF COLLOIDAL SOLUTIONS	172
Condensation Methods	172
Dispersion Methods	177

CHAPTER VII

PROPERTIES OF COLLOIDAL SOLUTIONS	182
General Properties	182
Viscosity	190
Color	196
Electrical Properties	206
Stability of Colloidal Solutions	212

CHAPTER VIII

GELS AND GELATINOUS PRECIPITATES.	236
Structure	236
Vapor Pressure Relations	245
Diffusion	258

CHAPTER IX

EMULSIONS AND FOAMS	260
Emulsions	260
Foams	268

CHAPTER X

NON-AQUEOUS COLLOIDAL SOLUTIONS	274
---	-----

CHAPTER XI

FOG AND SMOKE	276
Fog	276
Smoke	286
Precipitation of Solid	300

CHAPTER XII

GASES AND SOLIDS IN SOLIDS	304
Gases in Solids.	304
Solids in Solids	305

CHAPTER XIII

THICKNESS OF SURFACE FILMS	314
AUTHOR INDEX.	321
SUBJECT INDEX	333

APPLIED COLLOID CHEMISTRY

INTRODUCTION

In 1861 Graham¹ pointed out that substances like potassium hydroxide, potassium sulphate, magnesium sulphate, sugar, and alcohol diffuse much more rapidly in water than hydrous silicic acid, hydrous alumina, starch, dextrin, the gums, albumin, tannin, gelatine, etc. Since these latter substances occur usually in a non-crystalline or even gelatinous form, Graham suggested calling them colloids from the French word for glue. Substances which diffused rapidly were to be called crystalloids because many of them crystallized readily. Graham believed that the distinction between a crystalloid and a colloid was fundamental and was due to some molecular condition. Though modern colloid chemistry begins with Graham,² his distinction between crystalloids and colloids has been dropped. A colloidal substance is not necessarily amorphous, for colloidal gold is certainly crystalline at times and possibly always. We now speak of a colloidal state instead of a colloidal substance, and we call any phase colloidal when it is sufficiently finely divided or dispersed,³ without committing ourselves definitely as to what degree of subdivision is necessary in any particular case. The subdivided phase is often called the internal or dispersed phase and the enveloping phase the external phase or the dispersing phase. In fog the rain drops are the dispersed phase and the air the dispersing phase, while the solid particles are the internal phase in the case of smoke. When a milky liquid is obtained by precipitating barium sulphate in the cold, the barium sulphate is the dispersed

¹ Phil. Trans. **151**, 183 (1861); Jour. Chem. Soc., **15**, 216 (1862); **17**, 318 (1864).

² Interesting work was done by Selmi in 1844; but it had no appreciable effect on the development of scientific thought.

³ Cf. Wolfgang Ostwald: Grundriss der Kolloidchemie, 79 (1909).

phase and the solution the dispersing phase. In emulsions of oil in water, the oil is the internal phase because it is present in drops. When benzene is emulsified to a solid jelly in a small amount of soap and water, we have a mobile liquid as dispersed phase in a viscous mass. Bread or Ivory soap might be considered as a system with air as internal phase, and a fairly solid external phase. In a porous plate or a fine sponge the two phases are, or may be, continuous and it is therefore better to classify these as interlacing systems. True ruby glass consists of gold as dispersed phase in glass as a non-crystalline dispersing phase. With salt colored by exposure to cathode rays, we have metallic sodium as internal phase in an external phase of crystalline sodium chloride.

Adopting the very flexible definition that a phase is called colloidal when it is sufficiently finely divided, colloid chemistry is the chemistry of bubbles, drops, grains, filaments, and films, because in each of these cases at least one dimension of the phase is very small. This is not a truly scientific classification because a bubble has a film round it and a film may be considered as made up of coalescing drops or grains. It is a convenient classification, however for many purposes. At first sight colloid chemistry may not seem to be an important branch of chemistry, either theoretically or technically; but this opinion changes when we consider that a knowledge of colloid chemistry is essential to anybody who really wishes to understand about: cement, bricks, pottery, porcelain, glass, enamels; oils, greases, soaps, candles; glue, starch, and adhesives; paints, varnishes, lacquers; rubber, celluloid, and other plastics; leather, paper, textiles; filaments, casts, pencils, and crayons; inks; roads, foundry cores, coke, asphalt; graphites, patines; zinc, phosphorus, sodium, and aluminum; contact sulphuric acid, hardened oils, etc.; beer, ale, and wine; cream, butter, cheese, and casein products; cooking, washing, dyeing, printing; ore flotation, water purification, sewage disposal; smoke prevention; photography; wireless telegraphy; illuminants; comets; pharmacy; physiology. In other words, colloid chemistry is the chemistry of every-day life.

CHAPTER I

ADSORPTION OF GAS OR VAPOR BY SOLID

ADSORPTION OF GAS OR VAPOR BY SOLID

In an extremely subdivided phase, the surface is very large relatively to the mass of the phase and it is therefore advisable to discuss the properties of surfaces, beginning with the behavior of solids in contact with gases or vapors. All solids tend to adsorb, or condense upon their surface, any gases or vapors with which they are in contact. The amount of adsorption for given conditions of pressure and temperature varies with the nature and physical state of the solid and with the nature of the gas; in other words, ~~the adsorption is specific or selective~~. With the same solid and the same gas the amount of adsorption is greater the higher the pressure of the gas and the lower the temperature. Hunter¹ showed that many different gases and vapors are adsorbed by charcoal to a marked extent. While his experiments are probably not very accurate, and are not made at strictly comparable temperatures and pressures, they cover more ground than those of anybody else. Some of his data are given in Table I. In Table II are some data by Dewar² with cocoanut charcoal at low temperatures. The volumes of gas adsorbed have been calculated back to standard conditions; in other words to the volumes which the adsorbed gases would occupy at 0° and 760 mm pressure. Thus at -185° and 760 mm the actual volumes of gas adsorbed would be only 88/273, or approximately one-third, of the values given in Table II. This correction was not applied by Hunter in his work.

¹ Phil. Mag. (4) **25**, 364 (1863); Jour. Chem. Soc., **18**, 285 (1865); **20**, 160, (1867); **21**, 186 (1868); **23**, 73 (1870); **24**, 76 (1871); **25**, 649 (1872).

² Proc. Roy. Soc., **74**, 124 (1904).

APPLIED COLLOID CHEMISTRY

TABLE I.—ADSORPTION OF GASES AND VAPORS BY COCOANUT CHARCOAL

Volumes gas adsorbed per volume charcoal.

Temperature in Celsius degrees.

Pressures in millimeters of mercury.

Gas	Vol	Temp.	Press	Gas	Vol	Temp	Press
Acetic acid	83	159	676	Acetaldehyde	67	155	687
Water	24	159	24	Acetaldehyde	139	100	681
Water	44	128	624	Ammonia	22	127	655
Benzene	59	130	646	Ammonia	83	70	760
Ethyl alcohol	84	160	663	Ammonia	88	60	760
Ethyl alcohol	111	127	644	Ammonia	96	50	760
Ethyl alcohol	141	100	652	Ammonia	114	40	760
Ethyl acetate	72	154	639	Ammonia	149	20	760
Carbon tetrachloride	4	155	695	Ammonia	176	0	760
Carbon tetrachloride	8	100	636	Cyanogen	87	70	760
Methyl alcohol	61	159	684	Cyanogen	92	60	760
Methyl alcohol	127	129	663	Cyanogen	96	50	760
Methyl alcohol	151	100	652	Cyanogen	99	40	760
Chloroform	21	159	660	Cyanogen	107	20	760
Chloroform	30	100	651	Cyanogen	114	0	760
Acetone	68	157	671	Hydrochloric acid	60	100	668
Acetone	105	100	642	Nitrous oxide	64	100	661
Carbon bisulphide	91	158	659	Carbon dioxide	17	127	687
Carbon bisulphide	117	100	671	Carbon dioxide	71	0	760
Ethyl ether	54	160	684	Nitrogen	15	3	760
Ethyl ether	68	128	661	Hydrogen	4	3	760
Ethyl ether	87	100	644				

TABLE II.—ADSORPTION OF GASES BY COCOANUT CHARCOAL

Volumes gas adsorbed per volume charcoal.

Pressures not given; volumes corrected to 0° and 760 mm.

Temperature in Celsius degrees.

Gas	Vol	Temp	Gas	Vol	Temp.
Argon	12	0	Nitrogen	15	0
Argon	175	-185	Nitrogen	155	-185
Oxygen	18	0	Hydrogen	4	0
Oxygen	230	-185	Hydrogen	135	-185
Carbon monoxide	21	0	Helium	2	0
Carbon monoxide	190	-185	Helium	15	-185

In Table III are given some more recent data by Hempel and Vater,¹ who used a special animal charcoal, which they mixed to

¹ Zeit. Elektrochemie, 18, 724 (1912).

ADSORPTION OF GAS OR VAPOR BY SOLID

a stiff paste with ox-blood diluted tenfold with water and which they then charred at 600°.

TABLE III.—ADSORPTION OF GASES BY SYNTHETIC CHARCOAL

Volumes gas adsorbed per volume synthetic 600° charcoal.

Volumes probably corrected to 0° and 760 mm.

	+20°	-78°	-185°		+20°
H ₂	7 3	19 5	284 7	H ₂ S	213 0
N ₂	21 0	107 4	632 2	Cl ₂	304 5
CO	26 8	139 4	697 0	NH ₃	197 0
O ₂	25 4	122 4	SO ₂	337 8
	+20°	-78°		+20°	-78°
Ar	12 6	92 6	CH ₄	41 7	174 3
NO	103 6	231 3	C ₂ H ₄	139 2	360 7
N ₂ O	109 4	330 1	C ₂ H ₆	119 1	275 5
CO ₂	83 8	568 4	C ₂ H ₂	135 8	488 5

TABLE IV.—BOILING-POINTS OF VARIOUS LIQUIDS

Liquid	B. Pt.	Liquid	B. Pt.	Liquid	B. Pt.
He.	-268 7	C ₂ H ₆	-84	CH ₃ CHO	+20 8
H ₂	-252 6	HCl	-82 9	(C ₂ H ₅) ₂ O	+34 6
N ₂	-195 7	C ₂ H ₂	-82 4 ¹	CS ₂	+46 2
CO	-190	CO ₂	-79 ¹	Br ₂	+58 6
Ar.	-186 1	H ₂ S	-60 2	CHCl ₃	+61 2
O ₂	-182.8	Cl ₂	-33 7	CH ₃ OH	+64.7
CH ₄	-164	NH ₃	-33 5	CCl ₄	+76.7
NO	-153	(CN) ₂	-21	C ₂ H ₅ OH	+78.4
C ₂ H ₄	-105	SO ₂	-10	C ₆ H ₆	+80.2
N ₂ O	- 89 8			H ₂ O	+100.0

For purposes of reference there are given in Table IV the boiling-points of some of the substances whose adsorption by carbon has been studied. As a first approximation it is often stated that a gas or vapor is adsorbed more readily the higher its boiling-point. Thus helium is taken up by charcoal much less than hydrogen, and hydrogen again is adsorbed to a much less extent

¹ Sublimation point.

than nitrogen or oxygen. Carbon dioxide is adsorbed less readily than ammonia, so that these substances follow the empirical rule. Argon, however, is adsorbed less completely by charcoal than is nitrogen, while carbon monoxide is adsorbed to a greater extent at 0° than either argon or oxygen, though according to the rule this ought not to be so. Nitrous oxide is adsorbed less strongly than ethylene, and nitric oxide more strongly than methane, which is not according to the boiling-points. Ethane, ethylene, and acetylene are adsorbed more at $+20^\circ$ than is carbon dioxide, though the last is the most readily condensable gas of the four. The difference between carbon dioxide and hydrogen sulphide is in the right direction; but seems out of all proportion to the difference in boiling-points. Hydrogen sulphide is adsorbed more than ammonia, which is wrong; and chlorine is adsorbed much more strongly than ammonia, although the two boiling-points are practically identical. Cyanogen is adsorbed more than ammonia at 70° and less at 0° . In the case of vapors there is no relation between boiling-point and adsorption. Going from higher to lower boiling-points, we have the order: water, benzene, ethyl alcohol, carbon tetrachloride, methyl alcohol, chloroform, ether, and aldehyde. The order from greater to lesser adsorption is methyl alcohol, ethyl alcohol, aldehyde, ether, benzene, water, chloroform, and carbon tetrachloride. The truth of the matter is that adsorption is specific and varies with the nature of the gas and of the adsorbing solid. One charcoal is not like another. In Table V are Hunter's results on charcoal

TABLE V.—ADSORPTION OF GASES BY CHARCOAL FROM DIFFERENT WOODS

Volumes gas adsorbed per volume charcoal.

Temperature = 0°C , pressure = 760 mm.

Wood	Vol NH_3	Vol CO_2	Vol $(\text{CN})_2$	Wood	Vol NH_3	Vol CO_2	Vol. $(\text{CN})_2$
Logwood.	111	55	87	Jamaica logwood	69	33	
Ebony . . .	107	47	90	Sapan wood ..	70	32	
Camwood.. . .	91	45		Beech. . . .	58		
Green ebony	90	41		Rosewood.. .	51		
Fustic (Cuba)	90	58		Wistaria sinensis	44		
Lignum vitæ	89	47		Vegetable ivory		50	57
Boxwood	86	31	29	Cocoanut shell	176	71	114

made from different woods. The cocoonut charcoal has the greatest adsorbing power of all and, of the others, logwood charcoal has the greatest adsorbing action on ammonia, fustic charcoal on carbon dioxide, and ebony charcoal on cyanogen. It is not the most porous charcoal in the ordinary sense which adsorbs the most gas, because Hunter says that the charcoal made from the shell of the cocoonut is very dense and brittle. The pores are quite invisible and, when the charcoal is broken, the fracture presents a semi-metallic lustre. It has been suggested by De Saussure¹ that charcoals with very many pores of very small diameter are the best adsorbers because they present the largest surfaces for condensation. This is not quite right because there are other factors besides the extent of surface, among them the arrangement of the surfaces. A plane surface will adsorb a given amount of a gas under standard conditions, but two plane surfaces placed close to each other will apparently adsorb a good deal more gas than the same surfaces would if each did not re-enforce the other and modify the concentration gradient. The adsorption depends not only on the surface but on the structure also of the adsorbing material. Narrow pores, down to a certain limit, should adsorb more than spherical pores of large diameter and this actually happens. Table VI shows the change in the adsorption of air² when different charcoals are heated from -100° to $+500^{\circ}$. In a number of cases the parallelism between density and adsorption holds but by no means in all cases. While there may be an actual difference in the amount of surface, we are undoubtedly dealing with another factor, the presence in the charcoal of substances which affect the adsorption. Charcoal is far from being pure carbon and the great improvements in charcoal as used in warfare have been along the line of cleaning the charcoal very thoroughly in addition to increasing the surface. While cocoonut charcoal is usually considered the best, the sour cherry charcoal in Table VI does better; and the synthetic charcoal of Hempel and Vater³ was better than the best cocoonut charcoal which could then be obtained, though far inferior to the best cocoonut charcoal of today. The varying

¹ Cf. DEWAR: Proc. Roy. Inst., **18**, 180 (1905).

² PRUTTI and MAGLIA: Gazz. chim. ital, **40** I, 569 (1910).

³ Zeit. Elektrochemie, **18**, 724 (1912).

behavior of charcoal from cocoanut shell, logwood, fustic, and ebony is probably due to the presence of different impurities which affect different gases in different ways.

TABLE VI.—BEHAVIOR OF DIFFERENT CHARCOALS

		Apparent density	cc gas per cc charcoal — 100° to +550°	
			Air	Cl ₂
<i>Prunus cerasus</i> ..	Sour cherry ¹	1.6393	280 1	312 7
<i>Cocus nucifera</i> .. .	Cocoanut ¹	1.4497	251 8	334 2
<i>Phillyrea media</i> ...	Jasmine box... ..	1.4970	222 4	260 0
<i>Grevillea robusta</i> ..	Silk oak	1.4383	212 7 ²	
<i>Abies alba</i>	White spruce .	1.1901	199 5	
<i>Castanea vesca</i> .	European chestnut	1 3000	186 3	
<i>Buxus sempervirens</i>	Common box .	1 4192	138 5	
<i>Liospunos kaki</i> . . .	Chinese persimmon.	1.3398	134 5	
<i>Populus nigra</i>	Black poplar... .	1.2802	134 1	
<i>Prunus virginiana</i> .	Choke-cherry .	1.2359	133 0	
<i>Ceratonia siliqua</i> .	Carob ¹	1.6274	131 5	
<i>Prunus armeniaca</i>	Apricot ¹ ..	1.3994	129 5	
<i>Juglans regia</i> . . .	English walnut .	1.3132	118.6	
<i>Pinus rigida</i>	Pitch-pine ..	1.3114	111 1	
<i>Robinia pseudo-acacia</i>	Common locust .	1.2218	99 9	

Charcoal is used in most gas masks, because it is the best all-round adsorbent for toxic gases.² The removal of the toxic materials must be surprisingly complete. The adsorbent must be capable of reducing the concentration of the toxic gas from, say 1000 p.p.m.³ to 1 p.p.m. or less within the 0.1 second that the air takes in passing through the canister. This is accomplished with a safe margin by the present gas mask materials. In fact it has been shown that charcoal will reduce a concentration of 7000 p.p.m. of chloropicrin, CCl₃NO₂, in a rapidly moving current of air to less than 0.5 p.p.m. in something under 0.3 seconds.

Some use has been made in peace times of the fact that properly

¹ Shells and kernels.

² LAMB, WILSON and CHANEY: Jour. Ind. Eng. Chem., 11, 420 (1919).

³ Parts per million by volume.

ADSORPTION OF GAS OR VAPOR BY SOLID

prepared charcoal will adsorb gases to a considerable extent. Melsens¹ placed wood charcoal, saturated with dry chlorine, in the longer branch of a bent sealed tube and dipped that end of the tube into boiling water, while the shorter branch was placed in a freezing mixture. A portion of the gas was volatilized and the pressure thus developed caused liquefied chlorine to appear in the cold portion of the tube. Sulphur dioxide, hydrogen sulphide, hydrobromic acid, and cyanogen can be liquefied in the same way; but not bromine, hydrochloric acid, carbon bisulphide, ether, or alcohol.

In 1874 Tait and Dewar² described the use of charcoal as a means of getting a high vacuum. They placed a piece of charcoal in a tube having platinum electrodes, heated the tube to a red heat, exhausted it with a Sprengel pump and sealed it. If the tube was cool, no spark would pass when using an induction coil capable of giving a quarter of an inch spark. On heating the tube slightly some gas was given off from the charcoal and the spark passed. By making use of the increased adsorption at low temperatures quite surprising results were obtained.³ A bulb of 300 cc capacity, containing air at 15° and an initial pressure of 1.7 mm, was connected with another bulb holding five grams of charcoal. When the charcoal was cooled in liquid air, the pressure dropped to 0.00005 mm. A Crookes radiometer tube, filled with hydrogen at atmospheric pressure, had a charcoal bulb attached. On dipping the charcoal bulb into liquid air, no rotation took place even when the beam from an electric arc was focussed on the vanes. The motion became quite rapid however when the charcoal bulb was placed in liquid hydrogen because the adsorption of hydrogen by charcoal is sufficient at these very low temperatures, though not at the temperature of liquid air. The adsorption of helium by charcoal at -252° is not enough to make this experiment successful when the radiometer tube is filled with helium.

Since different gases are adsorbed in different amounts, the ratio of two gases in the charcoal will differ from the ratio in the gas phase and a separation will be possible to some extent.

¹ Comptes rendus, **77**, 781 (1873); Jour. Chem. Soc., **27**, 120 (1874).

² Proc. Roy. Soc. Edin., **8**, 348, 628 (1874).

³ DEWAR: Proc. Roy. Inst., **18**, 437, 756 (1906).

Dewar¹ heated about 50 grams of charcoal and then saturated it at -185° in a current of pure dry air at atmospheric pressure, at 76 mm, and at 5 mm. The vessel containing the charcoal was taken out of the liquid air and the temperature allowed to rise to 15° . The volumes of gas given off were 5.7, 4.8, and 4.5 liters respectively and the oxygen concentration varied irregularly between 56 and 58 percent. These experiments show the practical constancy of the mean composition of the gases adsorbed by the charcoal under the conditions of these experiments and they therefore show that wide changes in the pressure of the air current have but slight effect in altering the relative proportions of the adsorbed gases. In another experiment the vessel containing the saturated charcoal was placed in a vacuum vessel containing a little liquid air so that the temperature might rise slowly. This made it possible to collect and analyze separately the successive liters of gas as evolved. The data are given in Table VII. The mean composition of the six liters was 56 per-

TABLE VII.—DISTILLATION OF AIR ADSORBED BY CHARCOAL

First liter .	18.5 percent O ₂	Fourth liter.	72.0 percent O ₂
Second liter	20.6 percent O ₂	Fifth liter . .	79.0 percent O ₂
Third liter.	53.0 percent O ₂	Sixth liter .	84.0 percent O ₂

cent oxygen. A few experiments were also made with special mixtures of nitrogen and oxygen. When a gas mixture containing 6.5 percent oxygen was used and the charcoal was heated rapidly to 15° , five liters of gas were obtained, containing 23 percent oxygen.

At higher temperatures the results seem to be quite different, though this may be due to the removal of oxygen by combustion. Skey² found that red-hot charcoal retains over three volumes of nitrogen which is given off when the cooled charcoal is immersed in water. Storey and Lewis³ state that it is difficult to remove adsorbed nitrogen and carbon dioxide from coke even by heating

¹ Proc. Roy. Soc., **74**, 126 (1904); Proc. Roy. Inst., **18**, 184 (1905).

² Chem. News, **15**, 15, 27 (1867).

³ Am. Chem. Jour., **4**, 409 (1883).

the containing flask to 200° and exhausting with a Sprengel pump. In these two cases the oxygen was probably burned completely. It is not so easy, however, to account for Blumtritt's results.¹ He heated various forms of charcoal under mercury to 140° in a paraffin bath and analyzed the gases which were given off. With common wood-charcoal the gas was pure nitrogen. After the same charcoal had been moistened and dried, the evolved gas contained 85.6 percent N₂, 2.1 percent O₂, 9.2 percent CO₂, and 3.1 percent CO. The gas from poplar charcoal consisted of 83.5 percent N₂, and 16.5 percent CO₂, that from crushed alder charcoal had the composition 78.9 percent N₂ and 21.1 percent CO₂, while charcoal made from ash yielded a gas consisting of 76.0 percent N₂, 9.1 percent CO₂, and 14.9 percent O₂. These variations, if real, probably depend on the nature and amount of the hydrocarbons left in each charcoal; but the experiments should be repeated. Craig² heated a Jena flask filled with lignite coke to redness, closed the flask and analyzed the contents. The unadsorbed gas was nearly pure nitrogen and so was the adsorbed gas, which meant that the oxygen had oxidized some unspecified hydrocarbon without burning it to CO or CO₂.

In Dewar's experiments the oxygen adsorbed at -185° was apparently given off at -15° without any appreciable contamination with CO or CO₂. Calvert³ observed no reaction at ordinary temperatures, when carefully purified pieces of boxwood charcoal were heated to redness and, while still red-hot, were introduced into a cylinder standing over mercury and containing a measured volume of oxygen. Passing through the mercury undoubtedly cooled the charcoal a great deal before it came in contact with the oxygen. By special experiments Calvert satisfied himself that no carbonic acid had been formed, or existed, in the cube of charcoal. Since the adsorbed oxygen oxidized ethyl alcohol to acetic acid, and ethylene to carbon dioxide and water, it is certain that there cannot have been a serious error in analysis, because such oxidations could not be caused by carbon monoxide or carbon dioxide.

¹ Jour. prakt. Chem., **98**, 418 (1886).

² Chem. News, **90**, 109 (1904).

³ Jour. Chem. Soc., **20**, 293 (1867).

Quite different results were obtained by C. J. Baker¹ working with purified blood charcoal which was allowed to adsorb oxygen at -15° and was then pumped out. On heating the tube to 100° seven volumes of CO_2 were obtained when moist oxygen was used, while no gas was given off when dry oxygen was used. In a check experiment it was shown that no carbon dioxide was formed when water vapor and carbon were heated to 100° in a sealed tube for a week. The question arose whether dry oxygen was adsorbed or whether it was held more firmly than moist oxygen. Practically no gas was given off up to 350° . At 450° a regular stream of gas was given off which consisted of 99 percent CO and 1 percent CO_2 in those cases where the drying had not been done so carefully. Intermediate values were found for intermediate degrees of drying. Rhead and Wheeler² do not confirm Baker's results though this may be because they did their experiments differently. Rhead and Wheeler treated purified carbon at some definite temperature, 200° , 300° , etc., with air, pumped out the air, and then heated the charcoal more or less rapidly to 1100° and analyzed the gas. With an initial temperature of 300° and rapid heating to 1100° the composition of the evolved gas was 11.3 percent CO_2 and 88.4 percent CO when dried air was used, and 15.4 percent CO_2 plus 84.4 percent CO when moist gas was used. When the initial temperature was 300° , the gas coming off between 300° and 400° was composed of 57.0 percent CO_2 and 42.4 percent CO; between 400° and 500° the composition was 41.6 percent CO_2 and 58.0 percent CO, dropping to 0.8 percent CO_2 and 98.7 percent CO for the gas drawn off between 800° and 1100° . Baker found 1 percent CO_2 and 99.0 percent CO at 450° ; but his initial temperature was -12° . The two sets of experiments should be repeated so that we might know whether they are or are not contradictory. Neither Rhead and Wheeler nor Baker found any oxygen in the gas given off above 200° . By determining the oxidizing action at different temperatures of charcoal containing adsorbed oxygen, it should be possible to determine approximately at what temperature all the oxygen was converted into CO and CO_2 . In spite of all the excellent work that has been done on the com-

¹ Jour. Chem. Soc., **51**, 249 (1887).

² Ibid., **103**, 461, 1210 (1913).

bustion of carbon, there is still a great deal that we do not know. Hulett has found that there is a slow reaction between oxygen and charcoal at ordinary temperatures, apparently the formation of a non-volatile oxide.

When one blows a slowly dying wood fire with the bellows, the fire will often start burning briskly again, in spite of the fact that the large influx of cooler air must tend to chill the embers and thus to put the fire out. Bacon¹ suggests that the dying embers are covered with an adsorbed film of carbon dioxide which is swept away to some extent by the draught from the bellows. When the fire is burning briskly, there is less carbon dioxide adsorbed at the higher temperature and the natural draught is sufficient to bring oxygen to the burning wood. Though this hypothesis has not been proved, it is rendered more probable by the experiments of Arndt and Schraube,² who found that even at a red heat carbon dioxide is adsorbed more strongly than carbon monoxide or nitrogen. Manville's fluctuations of the ignition point of charcoal³ are probably due to hydrocarbons which had not been removed.

Ramsay⁴ has availed himself of Dewar's method of using cooled cocoanut charcoal as an adsorbent for gases to determine the amounts of neon and helium in the air. At 100° the oxygen, argon, and nitrogen are taken out practically quantitatively while the adsorption of neon and helium is negligible. At -185° practically all of the neon is adsorbed and none of the helium. From his observations, Ramsay concludes that the concentration of neon in the air is about 0.00123 volume percent and that of helium about 0.00044 volume percent, while the amount of free hydrogen cannot be greater than one five-hundredth of the combined volumes of the neon and helium. At great elevations this changes completely, the gas with the lowest molecular weight concentrating in the higher regions. Alleman⁵ gives some data for the estimated concentrations of hydrogen at different heights above sea-level, Table VIII.

¹ Jour. Phys. Chem., **17**, 768 (1913).

² Nernst Festschrift, 46 (1912).

³ Jour. Chim. phys., **5**, 297 (1907)

⁴ Proc. Roy. Soc., **76A**, 111 (1905); **80A**, 599 (1908).

⁵ Jour. Franklin Inst., **185**, 161 (1918).

TABLE VIII.—ESTIMATED DISTRIBUTION OF HYDROGEN IN THE ATMOSPHERE

Height in kilometers	Percent hydrogen	Height in kilometers	Percent hydrogen	Height in kilometers	Percent hydrogen
140	99.2	80	64.7	20	0.04
130	99.0	70	32.6	15	0.02
120	98.7	60	10.7	11	0.01
110	98.1	50	2.80	5	0.01
100	95.6	40	0.67		
90	88.3	30	0.16		

Dewar¹ has worked out a very effective lecture experiment, based on the selective adsorption by charcoal. A number of spectroscopic tubes, connected in series with a large U-tube containing charcoal are exhausted by cooling the charcoal until the electric discharge will barely pass. The charcoal tube is now placed in liquid air and a current of air is allowed to enter the system slowly, passing first through the charcoal tube which takes out the readily adsorbed gases such as oxygen, nitrogen, and argon, while helium, neon and hydrogen pass through. When the pressure in the first tube has risen sufficiently it begins to glow with the well-known rich orange hue of neon. In time the characteristic discharge of neon and helium appears in the other tubes. The sensitiveness of the neon tubes to induced electric oscillations from a coil of wire placed at right angles to the tube may be shown. Claude² points out that the remarkable luminosity of neon can be utilized for lighting purposes. One of the difficulties of the problem is the ease with which neon is masked by small quantities of certain other gases. It is not enough to introduce very pure neon into a tube with electrodes under suitable pressure in order to obtain an effectively luminous tube. This can be overcome by removing these other gases with cooled charcoal, when the beautiful orange luminescence of neon appears, and retains its brightness. The light is very rich in red rays and Claude considers it just the corrective required for the light of mercury vapor tubes.

¹ Proc. Roy. Inst., **18**, 444 (1906).

² Mon. Sci., **74**, 135; Jour. Franklin Inst., **171**, 624 (1911).

Krypton and xenon may be obtained from the air by means of cooled charcoal.¹ A current of air passes through a series of tubes immersed in liquid air for the purposes of purification, the last tube containing cotton wool in order to retain any dust of the solid, condensed impurities. This pure air is passed through a tube containing about 100 grams of charcoal for at least 24 hours. The charcoal tube is then removed and placed in solid carbonic acid, and the gas which is evolved is allowed to escape. The gas remaining in the charcoal at -78° is driven off by heating and exhaustion, and all the carbon compounds and oxygen removed from it. The remaining gas, consisting of nitrogen, krypton, and xenon, is separated into its constituents by condensation and fractionation. Instead of passing a current of air over charcoal at -183° , a few hundred grams of charcoal may be covered with liquid air and the latter may be allowed to evaporate in a silvered vacuum vessel. The gases remaining in the charcoal can then be separated as before. In this way spectrum tubes of krypton and xenon may be readily prepared.

Rutherford² found that cocoanut charcoal adsorbs radio-active emanations. A slow current of air charged with the emanations of radium, thorium, or actinium is deprived of some or all of its emanation in the passage through a tube filled with cocoanut charcoal, and for this purpose the charcoal need only be at ordinary temperature. The complete withdrawal of the emanation only takes place when the air is passed very slowly through the charcoal; if the speed is increased, the amount of unadsorbed emanation increases also. In another experiment Rutherford found that if a tube containing less than a gram of charcoal is connected to a vessel containing the emanation from several milligrams of radium bromide, the charcoal will adsorb the emanation in time. If some powdered willemite be mixed with the charcoal, the gradual adsorption is shown by the increasing brilliancy of phosphorescence of the willemite. It is not necessary to heat or exhaust the charcoal previously; but if this is done the emanation is adsorbed more rapidly. The charcoal retains the emanation at ordinary temperature but the greater

¹ VALENTINER and SCHMIDT: Sitzungsber. Akad. Wiss. Berlin, 1905, 816; DEWAR: Proc. Roy. Inst., 18, 445 (1906).

² Nature, 74, 634 (1906).

part of it is expelled by heating to a low red heat. Boyle¹ showed that cocoanut charcoal adsorbed thorium emanation the most and ordinary charcoal the least, while animal charcoal came in between the other two. The rate of adsorption increased very much when cocoanut charcoal was used at -75.5° and only slightly in the case of wood charcoal. At 211° cocoanut charcoal begins to give off carbon dioxide; but it shows some power of adsorbing thorium emanation up almost to 300° . It is not possible for the charcoal to become saturated with thorium emanation as may happen with other gases, because the thorium emanation adsorbed by the charcoal is decaying at the rate of half-value in 54 seconds.

The general rule for mixtures of gases seems to be² that the more readily adsorbed gas displaces the other to some extent and is adsorbed to a greater relative amount than one would have predicted from experiments on the single gases. This cannot be universally true. Bergter³ found that at pressures of 0.5 to 10 mm oxygen is adsorbed 30 to 40 times as strongly as nitrogen, and that at these pressures the presence of oxygen increases the amount of nitrogen adsorbed. With readily condensible gases, one may have one of the vapors helping to carry down the other. Cases of this sort have been studied by Hunter,⁴ the most striking instance being water and ammonia. It seems probable that the adsorbed water dissolves or adsorbs ammonia thus increasing the amount of ammonia apparently held by the charcoal. It has been shown by E. E. Reid that the presence of traces of benzene or ether in charcoal will increase the service time against chloropicrin.

The data in Table IX are not tabulated as one would like to have them; but they do indicate that the presence of a second gas will cut down the adsorption of the first,⁵ though such comparisons should be made at equal partial pressures. Passing one gas over charcoal which has adsorbed another gas should theo-

¹ Jour. Phys. Chem. **12**, 284 (1908); Phil. Mag. (6) **17**, 374 (1909). See also SATTERLY: Phil. Mag. (6) **16**, 584 (1908); **20**, 778 (1910), PORLEZZA and MORSI: Atti Accad. Lincei, **20** I, 932 (1911).

² FREUNDLICH: Kapillarchemie, 99 (1909).

³ Drude's Ann. **37**, 480 (1912).

⁴ Jour. Chem. Soc. **23**, 73 (1870).

⁵ HEMPEL and VATER: Zeit. Elektrochemie, **18**, 724 (1912).

ADSORPTION OF GAS OR VAPOR BY SOLID

retically cause complete displacement of the adsorbed gas; but it is evident that the effectiveness will be much greater if one displaces the slightly adsorbed gas by the readily adsorbed one rather than the other way round. It would be very interesting to determine an isotherm showing the relative amounts of two gases in the vapor phase and the charcoal phase when in equilibrium at constant pressure.

TABLE IX.—ADSORPTION OF MIXED GASES BY SYNTHETIC CHARCOAL

Mixed gases with 0.4 g synthetic 600° charcoal.
Could adsorb about 30 cc ethane.

cc H ₂	cc C ₂ H ₆	Percent C ₂ H ₆	cc gas adsorbed	Percent gas adsorbed	Percent C ₂ H ₆ unadsorbed
95 0	5 0	5	3.7	3.7	1 5
45.0	5 0	10	3 8	7 6	2 5
20 0	5 0	20	3 8	15 2	5.0
11.7	5.0	30	4 4	26 4	7 5
6 1	5.0	45	4 6	41.4	9.5
cc H ₂	cc CH ₄	cc gas adsorbed	cc H ₂	cc C ₂ H ₄	cc gas adsorbed
95 0	5 0	1.3	95 0	5.0	3 6
15 0	5.0	2.7	15 0	5 0	4 4
6 1	5 0	3.3	6 1	5 0	5 1
2 7	5 0	3 9	2 7	5.0	5.5
cc H ₂	cc C ₂ H ₂	cc gas adsorbed	cc N ₂	cc C ₂ H ₄	cc gas adsorbed
95 0	5 0	3.6	95 0	5 0	6.2
15 0	5 0	4 7	30 0	5 0	9.6
6 1	5 0	5 2	12 2	5 0	10 7
2 7	5 0	5 7	5 4	5 0	11 6

A curious case has been cited by Matwin.¹ Charcoal will take carbon bisulphide and carbonyl sulphide out of illuminating gas, one kilogram of charcoal cutting the sulphur content of ten cubic meters of gas to 2.92 grams. Porous charcoals are the best,

¹ Jour Gasbeleuchtung, 52, 602 (1909).

such as pine and linden. Bone-black takes up almost no carbon bisulphide, and cocoanut charcoal is said to be even less effective. This is very remarkable, because cocoanut charcoal adsorbs carbon bisulphide strongly. We must either assume that the illuminating gas cuts down the adsorption of carbon bisulphide very much or that there is an error in the statement. If carbon bisulphide and illuminating gas were adsorbed in the same ratio in which they occur in the mixture, there would be no apparent purification even though the actual adsorption were very large.¹ This point calls for more study.

The adsorption of gases by charcoal has been studied extensively, because charcoal adsorbs so many gases and adsorbs them so strongly. Experiments have also been made with many other solids—silica, alumina, glass, wool, rubber, celluloid, meerschaum, metals, soils, etc. The behavior of glass is important because of its use in the laboratory, Mulfarth² states that the adsorption decreases in the order: NH_3 , SO_2 , N_2O , C_2H_2 . Kundt and Warburg³ found that a small amount of water is retained obstinately by glass even when the pressure is reduced practically to zero. In order to remove this water the glass must be heated, in which case one is likely to cause changes in the glass, setting free water vapor and gases that were not adsorbed in any proper sense of the term.⁴ On the other hand, the film of water which usually covers glass surfaces is due chiefly to alkali dissolved from the glass.⁵ It is hard to tell whether the change in the vacuum of a Crookes' tube is due to adsorption of the gas by the glass or not. Swinton⁶ found that the inner surfaces of these tubes are roughened perceptibly after being subjected to cathode ray bombardment. When these portions of the tube are heated strongly in a blow-pipe, they immediately become clouded, owing to the formation of minute spherical bubbles which average about 0.01 mm in diameter. The centers

¹ Cf. LEIGHTON: *Jour. Phys. Chem.*, **20**, 32 (1916).

² Drude's *Ann.*, **3**, 328 (1900).

³ *Wied. Ann.*, **24**, 327 (1884); cf. BUNSEN: *Pogg. Ann.*, **156**, 201 (1875).

⁴ SHERWOOD: *Jour. Am. Chem. Soc.*, **40**, 1645; *Phys. Rev.* (2) **12**, 448 (1918).

⁵ WARBURG and IHMORI: *Wied. Ann.*, **27**, 481 (1886); IHMORI: *Ibid.*, **31**, 1006 (1887).

⁶ *Proc. Roy. Soc.*, **79A**, 134 (1907).

of the bubbles are about 0.12 mm from the inner surface of the glass. The number of bubbles per square centimeter of glass was found to be about 625,000, or about 0.000133 cc of gas per square centimeter. The gas is mostly hydrogen and is given off when the glass is powdered. It is not known whether the bubbles are connected with the inner part of the tube by minute channels or not. If they are, this is a case of adsorption. If the bubbles are actually buried in the glass owing to the latter flowing round them, that is not adsorption.

L. J. Briggs¹ showed that finely divided quartz adsorbs water vapor, though not to the same extent as amorphous silica. About 9 mg water was adsorbed at 30° by 50 g quartz having an estimated surface of 20,000 cm² when the vapor pressure was 26.1 mm, about 4.5 mg when the vapor pressure was 19.6 mm, and about 0.5 mg when the vapor pressure was 0.2 mm. Cohnstaedt² states that the gas given off by aluminum electrodes in a Crookes' tube is water vapor and not hydrogen, as usually believed. He claims to prove that glass and aluminum surfaces will retain water even when heated to 500° or when dried over phosphorus pentoxide. It is the presence of a water film of varying thickness on a glass or other vessel which makes it necessary to keep the moisture constant if accurate weighings are to be made. Professor Morley once said that it was a mistake to believe that it is a difficult matter to dry a gas. That is a very simple thing to do; but the difficulty is to dry the vessel which holds the gas.

Drucker and Ullmann³ showed that the adsorption of a vapor by the glass containing vessel causes only a negligible error in vapor-density determinations with ether, alcohol, benzene, and chloroform; but the error may amount to 2 percent with acetic acid at 80°. At higher temperatures the adsorption decreases and the error is considerably less. The adsorption of ammonia by solid ammonium hydrosulphide introduces a serious error in the equilibrium relations for ammonia and hydrogen sulphide.⁴

¹ Jour. Phys. Chem., **9**, 617 (1905)

² Drude's Ann., **38**, 223 (1912).

³ Zeit. phys. Chem., **74**, 567 (1910).

⁴ MAGNUSSEN: Jour. Phys. Chem., **11**, 21 (1907).

While most solids, even though porous, do not adsorb gases as much as charcoal, yet Dewar¹ reports that dry aluminum oxide shows a remarkable power of adsorbing air at low temperatures, one gram condensing some 70 cc at atmospheric pressure. The adsorption by alumina decreases very rapidly with decreasing pressure, and consequently alumina cannot be used as a means of obtaining high vacua. Meerschau and silica behave somewhat like alumina. On the other hand, high vacua can be obtained by means of copper powder.² Carbon dioxide³ and water vapor⁴ are both adsorbed strongly by alumina. Platinum black may take up 100 volumes of hydrogen and palladium nearly up to 3000 volumes of hydrogen,⁵ but it is not certain whether this hydrogen is all adsorbed or is partly dissolved. In gas analysis palladium, heated to 100°, is used to remove hydrogen. This is purely a question of rate because equilibrium is reached more rapidly at the higher temperatures. Paal and Hohenegger⁶ report on the adsorption of acetylene by palladium. Platinum black will take up more than 800 volumes of oxygen; but it seems certain that some of the platinum has been oxidized.⁷ Celluloid adsorbs carbon dioxide⁸ and rubber apparently adsorbs⁹ it and also other gases, though it is possible that we have true solution in the case of rubber. Wool¹⁰ adsorbs both hydrochloric acid and ammonia gas. Rohland¹¹ reports that unsaturated compounds are adsorbed by clay and oxygenated compounds by the oxides of silicon, aluminum, iron and titanium.

If the film of condensed air on a small particle remains of the same thickness irrespective of the diameter of the particle or if it does not decrease too rapidly with decreasing diameter, the ratio of air film to mass of particle will increase as the particle

¹ Proc. Roy. Inst., **18**, 435 (1906).

² MERTON: Jour. Chem. Soc., **105**, 645 (1905).

³ SCHEERMESSE: Centralblatt (3) **1**, 165 (1870).

⁴ JOHNSON: Jour. Am. Chem. Soc., **34**, 911 (1912).

⁵ PAAL and GERUM: Ber. deutsch. chem. Ges., **41**, 805 (1908).

⁶ Ber. deutsch. chem. Ges., **43**, 2684, 2692 (1910).

⁷ ENGLER and WÖHLER: Zeit. anorg. Chem., **29** (1909).

⁸ LEFEBURE: Jour. Chem. Soc. **105**, 328 (1914).

⁹ REYCHLER: Van Bemmelen Gedenkboek, 55 (1910).

¹⁰ FREUNDLICH: Kapillarchemie, 106 (1909).

¹¹ Zeit. anorg. Chem., **65**, 108 (1909).

grows smaller. Cushman and Coggeshall¹ found that a rock powder which would pass through a 200 mesh sieve surged like a liquid. When poured into a vessel, it only filled 46 percent of the space, while a coarser powder filled more. It is not surprising that the air-cushion around each particle makes the grains move one over another like a liquid. A similar phenomenon has been observed with ground phosphate rock. With a substance like carbon black, which adsorbs gases very markedly, as little as 5 percent of the apparent volume may be due to the carbon black² and a liter of carbon black may contain 2.5 liters of air.³ When indigo is reduced to a very fine powder by means of a disintegrator⁴ the single particles appear to be separated one from another by an envelope of air, so that the dry, solid powder occupies a space equal to that of a 20 percent paste of indigo, containing the same amount of indigo. Stoney⁵ points out that the freedom of motion of finely divided solid particles becomes more marked when there is a temperature gradient. He cites the mobility imparted to very fine powders such as magnesium carbonate or precipitated silica by heating them in a metal dish. When the dish is disturbed the powder glides about as if floating whenever the powder is able by radiation to maintain a lower temperature than the dish.

Ives, Kingsbury and Karrer⁶ state that the characteristics of thermocouples of varying diameter can be accounted for rather satisfactorily if it is assumed that they may be considered as cylindrical wires to which heat is conveyed through thin films of hot gas, of thickness independent of the temperature and size of the wire.

The presence of a film of air or vapor round a solid particle is shown in a striking way by the fact that it is quite a simple matter⁷ to pass suspended phosphorus pentoxide through several wash-bottles in spite of its tremendously hygroscopic nature.

¹ Jour. Franklin Inst., **174**, 672 (1912).

² CABOT: Eighth Int. Congress Applied Chem. **12**, 18 (1912).

³ SABIN: Technology of Paint and Varnish, 201 (1917).

⁴ Jour. Soc. Dyers and Colourists, **17**, 294 (1901).

⁵ Phil. Mag. (5) **4**, 443 (1877).

⁶ Jour. Franklin Inst., **186**, 421 (1918).

⁷ ENGLER and WILD: Ber. deutsch. chem. Ges., **29**, 1929 (1896).

Tyndall¹ found it very difficult to get experimental tubes which were absolutely clean on the surface and which contained no suspended particles. Dust-motes from the external air passed through U-tubes containing potash and sulphuric acid and through flasks containing ethers or alcohols. He states that it requires long-continued action on the part of an acid, first to wet the motes and then to destroy them.² The difficulty in stopping smokes in gas warfare is that the particles do not come in contact with the materials in the mask.

Schloesing³ has put the thing generally by saying that it is much easier to take gas out of a gaseous mixture than to remove suspended liquid or solid particles. If the sheath of adsorbed air or gas is removed, wetting may take place. Since the sulphur trioxide from the contact process can be caught in concentrated acid and not satisfactorily in water, the concentrated acid must displace the gas film rapidly and fairly completely, while water does not; but we do not yet know the reason for this. One cannot agree with Knietzsch⁴ however when he says that it is a very remarkable and not satisfactorily explained fact that the sulphuric acid fog from the burner gases is more difficult to precipitate when it is cooled rapidly than when it is cooled slowly. Rapid cooling gives smaller particles and the air-cushion is larger relatively to the mass; consequently precipitation is more difficult.

Schuster⁵ studied the disruptive discharge through gases and found an apparent diminution of dielectric strength with diminution of pressure. Since no sufficient decrease in inductive capacity could be observed in the mass of the gas, he assumed that layer in contact with the electrode there was a condensed surface of gas having a large inductive capacity. Schuster pointed out that some of the most puzzling facts of the disruptive discharge admit of explanation if we once admit the possibility of such a contact layer, diminishing in density with decreasing gas pressure. If this layer of adsorbed gas offers an increased resistance to the passage of an electrical discharge, it follows, from

¹ Phil. Trans., **160**, 337 (1870).

² See also EHRENBURG: Die Bodenkolloide, 226 (1915).

³ Comptes rendus, **94**, 1187 (1882).

⁴ Ber. deutsch., chem. Ges., **34**, 4081 (1901).

⁵ Phil. Mag. (5) **29**, 197 (1880).

the Theorem of LeChatelier, that an electrical stress will tend to remove the film of adsorbed gas. This enables us to account for many apparently unrelated facts. Electrical waves will tend to remove active oxygen or active hydrogen from an electrode and will therefore cut down the over-voltage.¹ Superposing an alternating current on a direct current also decreases the over-voltage, making other reactions possible.² The experiments of Margules³ and Ruer⁴ on the dissolving of platinum find their explanation in the cutting down of the over-voltage.⁵ With direct current there is oxidation to a higher and insoluble stage. With alternating current the over-voltage is decreased and little or none of the insoluble compound is formed. The electrolytic detector, the crystal detector, and the coherer, as used in wireless telegraphy, seem to owe their action to the partial or complete elimination of an air film by means of electrical stress. The essential difference between the coherer and the detector is that coalescence takes place readily in the former case and not in the latter.

It is interesting to note that Lenard⁶ found that mercury wets platinum only when a current is flowing. At other times there is evidently an air film. It has been claimed by Allen⁷ that the photo-electric fatigue of metals is due to a change in the surface film or gas or in the gas included in the metal (Hallwachs). It cannot be due to a chemical change such as oxidation; to a physical change such as roughening of the surface; to an electrical change in the formation of an electrical double layer (Lenard); or to a disintegration of the metal due to the expulsion of electrons by light (Ramsay and Spencer). The difference in the results

¹ ROTHMUND: *Drude's Ann.*, **15**, 193 (1904); BENNEWITZ: *Zeit. phys. Chem.*, **72**, 223 (1910).

² ARCHIBALD and VON WARTENBERG: *Zeit. Elektrochemie*, **17**, 812 (1911); REITTLINGER: *Ibid.*, **20**, 261 (1914); GHOSH: *Jour. Am. Chem. Soc.*, **37**, 33 (1915); STEPANOFF: *Chem. Abstracts*, **10**, 2431 (1916).

³ *Wied. Ann.*, **65**, 629; **66**, 540 (1898).

⁴ *Zeit. phys. Chem.*, **44**, 81, *Zeit. Elektrochemie*, **9**, 235 (1903); **11**, 10, 661 (1905); HABER: *Zeit anorg. Chem.*, **51**, 365 (1906).

⁵ REITTLINGER: *Zeit. Elektrochemie*, **20**, 261 (1914).

⁶ *Wied. Ann.*, **30**, 212 (1887).

⁷ *Phil. Mag.* (6) **20**, 564 (1910); cf. LENARD: *Drude's Ann.*, **8**, 196 (1902); **T2**, 490 (1903).

APPLIED COLLOID CHEMISTRY

obtained by Allen may be due to the fact that Allen worked at atmospheric pressure, while Robinson's measurements were made on electrodes at a high vacuum.¹

In cases of marked adsorption of gases it is interesting to determine what is the probable density of the adsorbed gas. Mitscherlich² calculated that, when carbon dioxide at atmospheric pressure and 12° is adsorbed by boxwood charcoal, the carbon dioxide occupies only one fifty-sixth of its original volume. Since this is a lesser volume than the same amount of carbon dioxide can occupy as a gas at this temperature, it is usually assumed that some of it has been liquefied. It is possible, however, to consider the carbon dioxide as present in the form of a highly condensed gas which has not liquefied. It might be interesting to study the behavior of carbon dioxide near the critical point in presence of charcoal. The magnitude of the heat of adsorption is an argument in favor of the actual liquefaction of the gas. Dewar³ has calculated the apparent density of some gases adsorbed by cocoanut charcoal at low temperatures. The data in Table X show that the densities are of the same order as those of the liquid gases and are greater in some cases. At higher temperatures the amount of adsorption would be smaller and the apparent condensation less.

TABLE X—DENSITY OF GASES ADSORBED BY CHARCOAL

Density in grams per cubic centimeter.

Gas adsorbed	Temperature of adsorption	Density of adsorbed gas	Density of liquefied gas
Carbon dioxide.	+15	0 70	0 80
Oxygen	-183	1 33	1.12
Nitrogen	-193	1.00	0.84
Hydrogen	-193	0 06	0.07
Hydrogen	-210	0 08	
Hydrogen	-252	0.11	
Helium	-258	0.17	(0.122)

¹ Phil. Mag. (6) 23, 255 (1912).

² Sitzungsber. Akad. Wiss. Berlin, 1841, 376.

³ Proc. Roy. Inst., 18, 438 (1906).

It is to be noticed that the vapor pressure of a film of adsorbed gas in an apparently liquefied state stands in no relation to the vapor pressure of a mass of the liquefied gas. The phase rule generalization that the vapor pressure is constant for the system, liquid and vapor at constant temperature, holds good explicitly only in case the disturbing effects due to gravity, distortion of the solid masses, and capillary tensions are eliminated. So soon as a liquid film becomes thin enough so that the liquid no longer has the properties of matter in mass, the vapor pressure need not remain constant. When we have an adsorbed liquid or liquefied gas, the vapor pressure will vary also with the nature of the adsorbing agent. The lowering of the vapor pressure is shown by the fact that oatmeal,¹ previously dried at high temperature, has been used instead of sulphuric acid to produce the freezing of water under the receiver of an air-pump. L. J. Briggs² showed that the weight of the water film condensed on the surface of quartz at 30° in an atmosphere within one percent of saturation is 26.6 mg per square meter as determined by drying at 110°. This corresponds to a calculated thickness of the water film of 26.6 $\mu\mu$ assuming the density of the film to be uniform and equal to unity. Neither assumption is absolutely accurate.

Since the amount of adsorption increases rapidly with falling temperature, adsorption must be accompanied by a marked evolution of heat. In Table XI the data not bracketted are by Favre.³ All the molecular heats of adsorption are higher than the corresponding heats of liquefaction. The abnormally high values for hydrogen in palladium and platinum cannot be due to dissociation into monatomic hydrogen, because that would be accompanied by an adsorption of heat. They may be due in part to an oxidation of hydrogen. Masson⁴ considers that the heat of adsorption of water vapor does not differ materially from the heat of liquefaction; but Dewar's data,⁵ Table XII, confirm those of Favre, and we know also that there is always a

¹ THOMSON: Phil. Mag. (4) **42**, 448 (1871).

² Jour. Phys. Chem., **9**, 617 (1905).

³ Ann. Chim. Phys. (5) **1**, 209 (1874).

⁴ Proc. Roy. Soc., **74**, 249 (1904).

⁵ DEWAR: Proc. Roy. Inst., **18**, 183 (1905).

APPLIED COLLOID CHEMISTRY

heat effect when porous solids are wetted by liquids.¹ This is probably due to an actual increase in the density of the adsorbed liquid.

TABLE XI.—MOLECULAR HEATS OF ADSORPTION AND OF LIQUEFACTION OF GASES

Adsorbing agent	Gas	Adsorption g cal per mol	Liquefaction g cal per mol
Platinum.. . . .	H ₂	46,200	(240)
Palladium	H ₂	18,000	(240)
Charcoal	NH ₃	5,900— 8,500	(5,000)
Charcoal	CO ₂	6,800— 7,800	6,250
Charcoal.. . . .	N ₂ O	7,100— 7,700	4,400
Charcoal.	SO ₂	10,000—10,900	5,600
Charcoal.	HCl	9,200—10,200	(3,600)
Charcoal.	HBr	15,200—15,800	(4,000)
Charcoal.	HI	21,000—23,000	(4,400)

Melsens² found that when 25 cc of different liquids were added to 10 grams of freshly ignited wood charcoal there was a rise of temperature of several degrees with ether, alcohol, and

TABLE XII.—MOLECULAR HEATS OF LIQUEFACTION AND ADSORPTION OF GASES

Charcoal as adsorbing agent at -185° (Dewar).

Gas	Adsorption g cal per mol.	Liquefaction, g. cal. per mol
Hydrogen	1600	238
Nitrogen.	3686	1372
Argon.....	3636	
Oxygen	3744	1664
Carbon monoxide	3416	

carbon bisulphide. When 97 grams of bromine were added to 11 grams of charcoal the rise of temperature was about 30° . Since a sudden compression of ten atmospheres raises the tem-

¹ Cf. POUILLET: *Ann. Chim. Phys.* (2) **20**, 141 (1822); CHAPPUIS: *Wied. Ann.* **19**, 21 (1883); MARTINE: *Phil. Mag.* (5) **47**, 329 (1889); **50**, 618 (1900); (6) **15**, 595 (1903); PARKS: *Ibid.* (6) **4**, 240 (1902); **5**, 517 (1903).

² *Ann. Chim. Phys.* (5) **3**, 522 (1874).

ADSORPTION OF GAS OR VAPOR BY SOLID

perature of water only $1/77$ of a degree he concluded that the rise of temperature of 1.16° when charcoal is wetted by water corresponds to a pressure of 893 atmospheres. Calculating in the same way he drew the conclusion that the force of adsorption is 3100 atmospheres for bromine, 13,090 for carbon bisulphide, 4620 for ether and 3080 for alcohol.

Gaudechon¹ obtained the data given in Table XIII for different liquids, with wood charcoal. Since the heat of liquefaction varies with the temperature, it is probable that the heat of adsorption of gases and vapors does also; but this point seems not to have received any special attention.

TABLE XIII.—HEAT EVOLUTION ON WETTING WOOD CHARCOAL
Gram calories per gram charcoal.

	g cal.		g. cal
Water	3.9	Acetone	3 6
Methyl alcohol	11.5	Chloroform	2 3
Ethyl alcohol	6.9	Ether	1 2
Propyl alcohol	5.6	Benzene	4 2
Amyl alcohol	3.7	CCl ₄	1 5
Formic acid	12.0	CS ₂	4.0
Acetic acid	6.0	C ₆ H ₁₂	0 4

Lamb and Coolidge² find that curves, which approximate closely to straight lines, are obtained when the heats of adsorption of the vapors of some organic liquids by charcoal are plotted against the amounts adsorbed. The difference between the heat of adsorption and the heat of vaporization is called by them the net heat of adsorption and is practically constant for the different liquids studied, when referred to equal volumes of adsorbed liquid. Assuming that this net heat of adsorption is a heat of compression, the attracting force is estimated to be about 37,000 atmospheres when one cubic centimeter of liquid is adsorbed by ten grams of charcoal.

The action of water vapor on cotton has been studied by

¹ Comptes rendus, **157**, 209 (1913).

² Jour. Am. Chem. Soc. **42**, 1146 (1920).

Beadle¹ and by Masson.² If the bulb of a thermometer be covered with carefully dried cotton wool, and if the bulb be then dipped in a beaker of water at the same temperature, the thermometer will rise 8°–12° or even more. The relatively large amount of air which is always entangled in the cotton wool does not escape during or after immersion, and the fibers present a glistening appearance under water, which suggest that they are not wetted completely. Medicated or absorbent cotton differs from the ordinary, nearly pure, material in that the former has been freed from traces of natural cotton wax by treatment with solvents. When absorbent cotton is dipped into water, the rise in temperature is less than in the previous case even though more water is taken up by the cotton. In the case of the nearly pure cotton wool, the water evidently distills across the air space, while there is a certain amount of direct wetting with the absorbent cotton. There should therefore be a marked evolution of heat if cotton is placed in saturated water vapor and the two cottons should behave exactly alike. Both these predictions were confirmed experimentally. Masson obtained similar results when gun cotton or glass wool was exposed to saturated water vapor or cotton to the vapor of absolute alcohol; but the heat effects were much smaller in these instances owing to the lesser adsorption.

L. B. Loeb³ finds that the adsorption of methyl alcohol vapor by 0.41g platinum black causes a rise of temperature of about 0.36° when there is no oxidation.

The effect of traces of impurity on the adsorption is shown in some experiments by Berliner.⁴ His purified palladium foil adsorbed about 860 volumes of hydrogen. If allowed to stand in a vacuum for an hour, it then adsorbed practically no hydrogen. If left for an hour or two in the air, the same thing happened. The disturbing factor is apparently a trace of grease, because water did not wet the soiled palladium. Similar results were obtained with platinum.

¹ *Nature*, **49**, 457 (1884); *Chem. News*, **71**, 1 (1895); **73**, 180 (1896).

² *Proc. Roy. Soc.*, **74**, 230 (1904); MASSON and RICHARDS: *Ibid.*, **78A**, 412 (1906).

³ *Proc. Nat. Acad. Sci.*, **6**, 107 (1920).

⁴ *Wied. Ann.*, **35**, 803 (1888).

THE ADSORPTION ISOTHERM

So far we have only committed ourselves to the qualitative statement that the amount of adsorption increases with increase of pressure. It is now advisable to consider the quantitative side. Dewar¹ has made some measurements with hydrogen at varying pressures in charcoal at -185° . The results are given in Table XIV. Dewar says in regard to them that the amount adsorbed is seen to increase with the pressure to 10 atmospheres, after which the adsorption in the pores of the charcoal seems to be independent of the pressure. At the temperature of liquid air this sample of charcoal (6.7 g) would not adsorb more than about one liter of hydrogen even when the pressure was raised from 10 to 25 atmospheres. It appears that Dewar considers the decrease from 156 cc to 138 cc as due to experimental error for he says distinctly that the adsorption had come to a limit. Since that time a number of careful investigations have been made on the quantitative variation of the adsorption with the pressure.²

TABLE XIV.—HYDROGEN ADSORBED BY CHARCOAL AT -185°

Atm	cc/gram	Atm	cc/gram
1	92	15	149
5	138	20	145
10	156	25	138

If we plot the amounts of adsorbed gas against the pressures, we get the so-called adsorption isotherm, a smooth curve concave to the pressure axis. Trouton³ obtained a curve with the opposite flexure for the adsorption of water by flannel; but Masson⁴

¹ Proc. Roy. Inst., **18**, 437 (1906).

² TRAVERS: Proc. Roy. Soc., **78A**, 9 (1906), DAVIS: Jour. Chem. Soc., **91**, 1066 (1907); GEDDES: Drude's Ann., **29**, 797, (1907); BOYLE: Jour. Phys. Chem., **12**, 484 (1908); Phil. Mag. (6) **17**, 377 (1909); MCBAIN: Ibid **18**, 916 (1909); Zeit. phys. Chem., **68**, 471 (1909); HOMFRAY: Ibid., **74**, 139, 687 (1910); TITOFF: Ibid., **74**, 641 (1910); PRUTTI AND MAGLIA: Gazz. chim. ital., **40** I, 569 (1910).

³ Proc. Roy. Soc., **77A**, 292 (1905).

⁴ Ibid., **78A**, 9 (1906)

obtained normal curves for water and cotton, and Travers¹ obtained normal curves for wool and cotton with water vapor, so that Trouton's results are apparently due to experimental

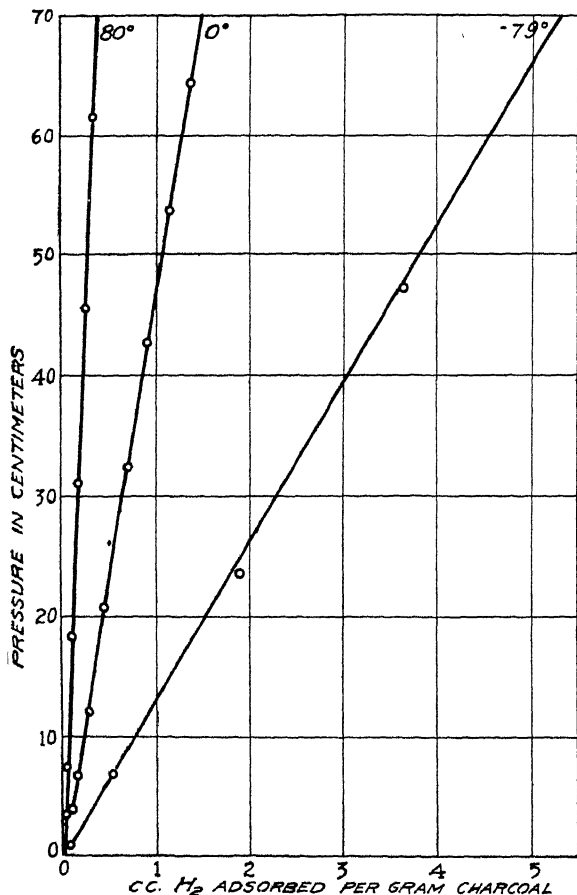


FIG. 1.

error. Trouton² also obtained an abnormal type of curve for the adsorption of water vapor by glass; but it seems probable that alkali dissolved from the glass has been a disturbing factor.

¹ Proc. Roy. Soc., **79A**, 204 (1906).

² Ibid., **79A**, 383 (1906).

ADSORPTION OF GAS OR VAPOR BY SOLID

If the gas is adsorbed but slightly, the curve may seem practically a straight line over the ordinary pressure ranges. This is shown very clearly in the curves for hydrogen in charcoal Fig. 1 as determined by Titoff.¹ If the gas is adsorbed strongly, the isotherm bends around so as to run nearly parallel with the pressure axis, because then a marked increase in pressure causes

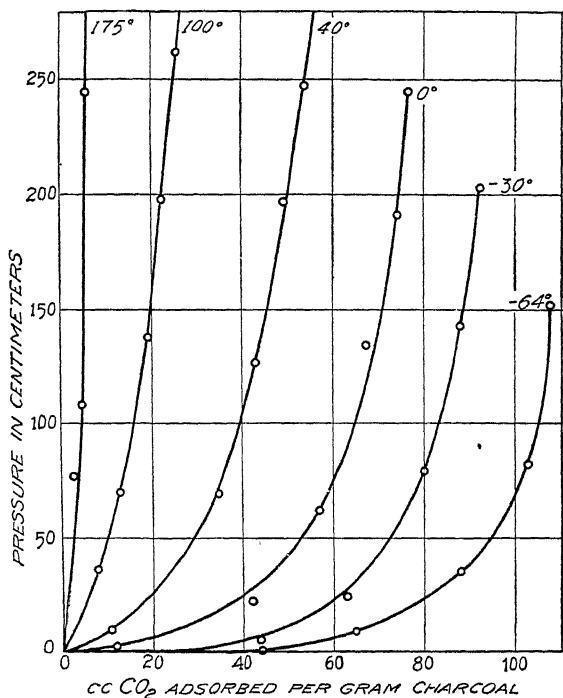


FIG. 2.

only a relatively slight increase in adsorption. These two extremes can be realized very well with ammonia and charcoal² at 175° and -64°, Fig. 2. In Table XV are given Titoff's data for the adsorption of ammonia by charcoal at 0° and at 151.5°. Under $\Delta x/\Delta y$ is given the mean increase in adsorption with increase of pressure between each two consecutive observations.

¹ Zeit phys. Chem., **74**, 641 (1910).

² RICHARDSON: Jour. Am. Chem. Soc., **38**, 1828 (1917).

At 0° the values drop from 92 to 3, a ratio of over 30:1, while at 151.5°, the drop is only from 51 to 11, a ratio of less than 5:1.

If we plot the logarithms of the amounts of adsorbed gas

TABLE XV—ADSORPTION OF AMMONIA BY CHARCOAL

Temperature 0°			Temperature 151 5°		
Pressure in mm	Adsorption in cc	$\Delta x/\Delta y$ cc/mm	Pressure in mm	Adsorption in cc	$\Delta x/\Delta y$ cc/mm
2 9	5 4	. . .	2 8	0 3	
28 8	30 2	0 92	16 6	1 0	0 051
78 7	60 4	0 65	64 8	2 1	0 021
161.0	90 3	0 36	176 2	4 0	0 018
319 2	115 7	0 16	285 0	5 5	0 013
490 0	127 0	0 07	432 7	7 2	0 012
636 4	132 4	0 04	576 8	8 9	0 012
746 7	135.9	0 03	721 8	10.5	0 011

against the logarithms of the pressures, we get a curve which approximates a straight line, especially if the gas is not adsorbed too much. This shows that the data can be represented approximately by an equation¹ of the form $(x/m)^n = kp$, where x is the

TABLE XVI.—ADSORPTION OF CARBON DIOXIDE BY CHARCOAL

Formula $x^{1.77}/p = 0.0602$.

x = cc CO₂ adsorbed per cc charcoal.

p = pressure in mm Hg. Temp. 31°.

p	x found	x calc	p	x found	x calc.
41 5	1 7	1 7	453	6 5	6 4
120	2 9	3.1	534	7.1	7 1
194	4 0	4 0	602	7 6	7.6
276	4 7	4.9	678	8 3	8 2
340.	5 4	5 5	698	8.6	8 3
405.	5.9	6.0	703	8 9	8.4

amount of gas adsorbed and m the amount of the adsorbing solid, while p is the pressure and k and n are constants to be determined experimentally for each temperature. The expo-

¹ Chemists are in the habit of calling this an exponential formula which is not correct in the strict mathematical sense; but which is justified by usage.

nential factor, n , is usually not an integer and its physical significance is unknown.¹ In Table XVI are given some data by Geddes² on the adsorption of CO_2 by charcoal. The formula enables us to calculate the adsorption with a moderate degree of accuracy. Of course data could have been picked out which would have looked better, but there seems no advantage in doing this. The formula cannot possibly represent the facts for pressures at which the curve runs nearly parallel to the pressure axis, and the experiments of Richardson³ on the adsorption

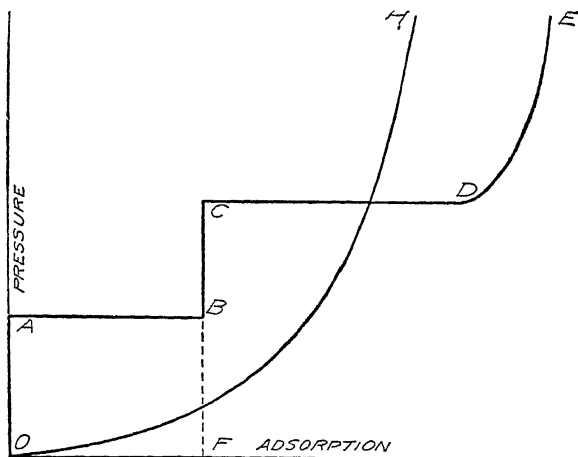


FIG. 3.

of ammonia by charcoal makes it probable that the equation never describes the facts accurately over any wide range of pressures. For the present it should be considered as a serviceable interpolation formula, though it may possibly belong in the same category as the simple gas law.

The fact that we get a smooth curve when plotting pressure direct against adsorption shows that no definite compound is formed. In Fig. 3 the pressure is plotted along the vertical axis and the amount of gas condensed on or by unit mass is

¹ For a slightly different formulation, see WILLIAMS: *Trans. Faraday Soc.*, **10**, 167 (1914); *Proc. Roy. Soc., Edinburgh*, **39**, 48 (1919).

² *Drude's Ann.*, **29**, 797 (1909).

³ *Jour. Am. Chem. Soc.*, **38**, 1828 (1917).

plotted along the horizontal axis. The typical adsorption isotherm is represented by the curve OH, while OABCDE is the curve (not to scale) for the taking up of water by sodium sulphate. Along OA the solid phase is anhydrous sodium sulphate. Along AB the pressure remains constant because three phases are present: Na_2SO_4 , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and water vapor. Along BC the pressures change without any more water being taken up and consequently there are only two phases, water vapor and the compound $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. The composition of the compound is given by F, the point at which the prolongation of CB cuts the axis of abscissas. Along CD the phases are $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, saturated solution and vapor, so the pressure remains constant, while unsaturated solution and vapor coexist along the curve DE. Many curves of this type have been determined by Browne¹ and others in his laboratory for the ammonia compounds. The curve OH is clearly not of this type and represents either a continuous series of solid solutions or an adsorption. The equilibrium is usually reached fairly rapidly, which is an argument against the existence of a solid solution though by no means a conclusive one. More convincing is the fact that the amount of adsorption by charcoal varies with the structure² and the extent of surface. The change produced by grinding charcoal³ is only a slight one, because the surface of the unground charcoal is so enormous. Lagergren⁴ estimates that one gram of charcoal has a surface of four square meters and is composed of about 1.4 billion particles. Lamb, Wilson and Chaney⁵ consider that one cubic centimeter of active war charcoal has a surface of about 1000 square meters (density about 0.4).

While the experiments on the taking up of gases by charcoal show fairly conclusively that surface phenomena are the important ones, there is always the possibility that a solid solution may also be formed to some extent. McBain⁶ considers that

¹ See BROWNE and HOULEHAN: *Jour. Am. Chem. Soc.*, **35**, 649 (1913).

² PRUTTI and MAGLIA: *Gazz. chim. ital.*, **40** I, 569 (1910).

³ CHAPPUIS: *Wied. Ann.*, **12**, 164 (1881). Cf. also GURWITSCH: *Zeit. Kolloidchemie*, **11**, 17 (1912).

⁴ See VAN BEMMEL: *Die Absorption*, 410 (1910).

⁵ *Jour. Ind. Eng. Chem.*, **11**, 420 (1919).

⁶ *Phil. Mag.* (6) **18**, 916; *Zeit. phys. Chem.*, **68**, 471 (1909).

over 18 percent of the hydrogen taken up by cocoanut charcoal at the temperature of liquid air is present as a solid solution.¹ On the other hand Titoff² believes that the amount of hydrogen dissolved in the charcoal has been over-estimated by McBain.³ The truth of the matter is that we have no definite criterion which will enable us to distinguish accurately in all cases between solid solution and adsorption. In the case of cellulose and of gelatine it is quite possible that some water is actually dissolved. Until we know more about the subject it is safer to treat any doubtful case as chiefly one of adsorption.

On the other hand, the two special cases of metals and rubber with gases call for some special comment. Assuming the existence of pores in platinum or palladium foil, one can account for the selective diffusion of hydrogen by postulating adsorption in the pores and subsequent diffusion. At high temperatures the adsorption would be much less, and it is difficult to explain the increased rate of selective diffusion. It is simpler to account for the diffusion of hydrogen through platinum by postulating that some of the hydrogen actually dissolves in the platinum. In that case the solubility should be independent of the physical structure of the platinum. This seems to be true within narrow limits for platinum and within wide limits for palladium. It seems probable that platinum can dissolve several volumes of hydrogen at ordinary temperatures, and palladium nearly eight hundred volumes.⁴ The bulk of the hundred volumes of hydrogen which are taken up by platinum black⁵ must be adsorbed, and the same must be true of the nearly 3000 volumes taken up by colloidal platinum.⁶ This is apparently the conclusion reached by Holt, Edgar, and Firth.⁷ If platinum and palladium dissolve hydro-

¹ Cf. TRAVERS: Proc. Roy. Soc., **78A**, 9 (1906).

² Zeit. phys. Chem., **74**, 641 (1910).

³ For other discussions, see MASSON: Proc. Roy. Soc., **74**, 251 (1904), DAVIS: Jour. Chem. Soc., **91**, 1066 (1907); GEDDES: Drude's Ann., **29**, 797 (1908); WÖHLER, PLUDEMANN and WÖHLER: Zeit. phys. Chem., **62**, 670 (1908); HOMFRAY: Ibid., **74**, 139, 687 (1910).

⁴ Cf. BOSE: Zeit. phys. Chem., **34**, 708 (1900).

⁵ RAMSAY, MOND and SHIELDS: Zeit. phys. Chem., **19**, 40 (1896); **25**, 657 (1898).

⁶ PAAL and GERUM: Ber. deutsch. chem. Ges., **41**, 805 (1908).

⁷ Zeit. phys. Chem., **82**, 513 (1913).

APPLIED COLLOID CHEMISTRY

gen to some extent, the passage of carbon monoxide through heated iron cannot be attributed to adsorption. At present it is not possible to say whether an iron carbonyl plays any part in the diffusion or not. In the case of platinum and oxygen Ramsay, Mond, and Shields¹ consider that most of the oxygen taken up forms $\text{Pt}(\text{OH})_2$. They point out that Thomsen obtained an evolution of heat of 17,000 calories for the reaction $\text{Pt} + \text{O} + \text{H}_2\text{O}$, while they find 17,600 calories for the so-called adsorption of sixteen grams of oxygen by platinum.

In view of the relative behavior of rubber with water and with pyridine, it is hard to see how the permeability can be a question primarily of adsorption. I think that we must assume that carbon dioxide, pyridine, etc., actually dissolve in rubber.

TABLE XVII.—ADSORPTION OF CARBON DIOXIDE BY BLOOD CHARCOAL

Formula $x/p = 0.00024$.

x = millimols CO_2 per gram charcoal.

p = partial pressure in mm Hg.

Temperature 20° .

p	x	k	p	x	k
613.1	0.1461	0.00024	337.7	0.0855	0.00025
611.1	0.1424	0.00023	325.5	0.0808	0.00025
605.	0.1320	0.00022	312.2	0.0706	0.00023
453.1	0.1014	0.00022	229.	0.0560	0.00024
437.2	0.1086	0.00025	221.2	0.0523	0.00023
435.2	0.1063	0.00024	176.	0.0452	0.00026
348.5	0.0844	0.00024	170.2	0.0451	0.00026
339.	0.088	0.00026		mean	0.00024

While the equation $x/m = kp$ is a special case of the equation $(x/m)^n = kp$, where $n = 1$, and therefore may hold even in cases of adsorption, it is also the simplest case of Henry's law for the solubility of gases in liquids. Reyhler² found that the amount of carbon dioxide taken up by blood charcoal was proportional to the partial pressure of the carbon dioxide in the vapor phase. The data are given in Table XVII. It does not

¹ Zeit. phys. chem., **25**, 684 (1898).

² Van Bemmelen Gedenkboek, 55 (1910).

ADSORPTION OF GAS OR VAPOR BY SOLID

seem probable that CO_2 dissolves in carbon, and I prefer to consider this a case of adsorption where the exponential factor happens to be unity. This view is confirmed by the fact that Geddes obtained very different relations for the adsorption of CO_2 by charcoal at 31° (Table XVI).

Reychler also found that the amount of carbon dioxide taken up by rubber was proportional to the pressure over a narrow range of pressures. This may well be a case of solution of carbon dioxide in rubber.

The concentration-pressure curve for hydrogen and palladium¹ has two ascending branches connected by a branch which is nearly but not quite, parallel to the concentration axis. It is not known to what extent the peculiarities of this curve are due to adsorption.

While many people are willing to speak of adsorption and to let it go at that, attempts have been made to account for adsorption either through the formation of known or unknown compounds. Rhead and Wheeler² consider that the fixation of oxygen by carbon involves the formation of a compound, C_xO_y , which breaks up into carbon dioxide and carbon monoxide when heated. Haber³ points out that, according to Bragg, the ordinary solid crystalline salts are not systems in which one anion and one cation form a molecule which is separated from the next; but that one anion is probably bound to all the surrounding cations. Unless the outer layer of a crystal differs fundamentally from the inner portions, there must be forces at the surface of the crystal similar to those acting between the outer layer and the next layer. If we call these forces chemical valences of some sort, it is possible that adsorption is due essentially to the saturation of these valences. These ideas have been developed by Langmuir⁴ as a result of his experiments on electrically heated carbon and other filaments in presence of oxygen at pressures of 0.004–0.007 mm. Langmuir considers that any crystal or

¹ HOITSEMA: *Zeit. phys. Chem.*, **17**, 1 (1895); RAMSAY, MOND, and SHIELDS: *Ibid.*, **19**, 25 (1896); HOLT, EDGAR and FIRTH: *Jour. Chem. Soc.*, **82**, 513 (1913).

² *Jour. Chem. Soc.*, **103**, 462 (1913).

³ *Jour. Soc. Chem. Ind.*, **33**, 50; *Zeit. Elektrochemie*, **20**, 521 (1914).

⁴ *Jour. Am. Chem. Soc.*, **37**, 1139 (1915); **38**, 1145, 2221 (1916).

any mass of liquid forms a giant molecule, and that an adsorbed gas forms a compound with the outer layer, the thickness of the reacting gas film being rarely over one or two molecules thick. Looking at the subject from a kinetic point of view he deduces an equation of the form

$$Q = \frac{1}{\frac{a}{p} + b - cp}$$

where Q is the amount adsorbed at the pressure p , and a , b and c are constants.

There are two independent questions involved in Langmuir's hypothesis, namely whether the maximum adsorption film is only one or two molecules thick and whether this layer forms a compound with the adsorbing agent. The first may be true and the second be wrong. Langmuir claims that the adsorbed film never exceeds two molecules in thickness for plane surfaces, though he is apparently willing to concede a greater thickness for porous substances. There is no question but that the adsorption film is very thin. Mitscherlich¹ calculates a thickness of about $50\mu\mu$ for carbon dioxide adsorbed by charcoal, and the film of water round each particle of clay² is usually assumed to be of the same thickness, while L. J. Briggs³ estimates about $27\mu\mu$ for the film of water on quartz. It is difficult to be certain on these points because one does not know the surface with any degree of accuracy; but the evidence is in favor of Langmuir's contention.

When it comes to the question of whether compounds are formed or not, it must be remembered that Langmuir uses the word molecule in a new sense. He considers that the oceans and all that in them is constitute one vast molecule and that catching a fish is a chemical reaction because it breaks up the molecule. This may be perfectly true; but the usefulness of it has not been made clear. For the present, it seems much wiser to say that one substance adsorbs another selectively, meaning that the concentration at the surface of the phase has increased. Whenever there is no proof that a compound is formed of the type at

¹ Sitzungsber. Akad. Wiss. Berlin, 1841, 379.

² Cf. DAVIS: Trans. Am. Ceramic Soc., 16, 69 (1914).

³ Jour. Phys. Chem., 9, 617 (1905).

ADSORPTION OF GAS OR VAPOR BY SOLID

present[†] recognized by chemists, it is safer not to postulate the existence of compounds. When the time comes that it is a distinct advantage to distinguish an entirely new type of compound, an indefinite chemical compound, that can be done; but hopeless confusion will arise whenever a man uses a word in one sense and his listeners in another. It is quite probable that a more careful study of contact catalysis may force us to adopt Langmuir's view or some modification of it; but it will then be necessary to gather in a lot of the loose ends.

In some cases compounds are undoubtedly formed. Thus when platinum black takes up oxygen, a portion of the oxygen is certainly present as oxide. On the other hand, it seems improbable that it would be so difficult to make carbon tetrachloride direct if the chlorine, which is adsorbed by charcoal and thereby made active,¹ consisted of a normal compound of carbon and chlorine. While the oxidizing action of platinum may be due to a platinum oxide, this cannot be true in the case of charcoal and oxygen. Calvert² showed that oxygen adsorbed by charcoal will oxidize ethyl alcohol to acetic acid and ethylene to carbon dioxide and water, reactions which certainly cannot be due to any known oxide of carbon. It also seems unsatisfactory to postulate that the noble gases form definite chemical compounds with charcoal.

Years ago Angus Smith³ ignored the variation of adsorption with the pressure and concluded that at atmospheric pressure charcoal adsorbed gases in volumes which were multiples of the volumes of hydrogen adsorbed. His figures were: hydrogen, 1; oxygen, 7.99; carbon monoxide, 6.03; carbon dioxide, 22.05; methane, 10.01; nitrous oxide, 12.90; sulphur dioxide, 36.95; nitrogen, 4.66. Smith lays stress on the fact that the 22 for carbon dioxide and the 10 for methane can be considered as $6 + 16$ and $6 + 4$ respectively, though it is difficult to see what this proves. In order to make the value for nitrogen seem plausible, Smith points out that $14 \times 4.66 = (14)^{\frac{1}{2}}$; but these calculations are only of historical interest now.

¹ DAMOISEAU: *Comptes rendus*, **73**, 60 (1876).

² *Jour. Chem. Soc.*, **20**, 293 (1867).

³ *Chem. News*, **18**, 21 (1868); *Proc. Roy. Soc.*, **28**, 322 (1879).

CHEMICAL REACTIONS

Since reaction velocity is probably directly proportional to the difference of chemical potential and inversely proportional to the chemical resistance, we can increase the reaction velocity either by increasing the difference of chemical potential or by decreasing the chemical resistance. The increased concentration due to adsorption at the surface of a solid will necessarily cause an increase in reaction velocity quite apart from any catalytic action which the solid may exert.¹ In the form of wood ashes, charcoal is often used in outhouses and elsewhere to eliminate unpleasant odors. The charcoal adsorbs the odorous substances and then accelerates their oxidation by oxygen which is adsorbed from the air. Shenstone² invented a respirator filled with powdered wood charcoal to be worn in hospitals and which should adsorb and then destroy germs of cholera and other diseases. This was the forerunner of the modern gas mask. It is not known whether the oxidizing action of the charcoal is due to anything more than the increase in concentration of the oxygen.

As a matter of fact, the effect of concentration seems to be relatively unimportant in most of the cases studied hitherto. Patrick's silica gel has a surface of 2.5×10^8 cm² per gram and is an excellent adsorbent, but, so far, it does not have any marked catalytic effect except in the oxidation of nitric oxide. It would be interesting to try this substance at 100° with the mixed vapors of alcohol and acetic acid, because this reaction takes place at a measurable rate in the vapor phase in the absence of any catalytic agent. It is stated that oxyhydrogen gas has been found to be quite stable under pressures of two thousand atmospheres, which shows that the catalytic action of platinum on mixtures of hydrogen and oxygen must be due to something more than a change in concentration. The marked difference in the behavior of platinum and charcoal toward oxyhydrogen gas is another argument in favor of the action of a catalytic agent being specific. On the other hand Hempel³ with SO₂ and O₂ obtained a yield

¹ See, however, LANGMUIR: Jour. Am. Chem. Soc., **38**, 2286 (1916).

² Pharm. Jour., **13**, 454 (1854).

³ Ber. deutsch. chem. Ges., **23**, 445 (1890).

of 65 percent SO_3 without any catalytic agent by working at a pressure of thirty to forty atmospheres.

If we have selective adsorption of the reaction products, this will cause a lowering of the chemical potential of the resultants¹ and will therefore increase the reaction velocity. It may even determine the direction of the reaction. Alcohol breaks down into acetaldehyde and hydrogen in presence of pulverulent nickel and into ethylene and water in presence of pulverulent alumina or silica.² Since nickel adsorbs hydrogen strongly and alumina adsorbs water,³ it seems natural to assume that the selective adsorption is the determining factor.⁴

While this seems very satisfactory, there are certain points which must not be overlooked. When making ethylene at Edge-wood Arsenal during the war, it was found advisable to have a large amount of steam present with the alcohol vapor in order to make temperature regulation easier. This undoubtedly decreased the rate of decomposition of the alcohol; but that difficulty was overcome by working at a higher temperature. It is very difficult to see how alumina can dehydrate alcohol in presence of a large amount of water vapor if the reason the alumina acts is because of its strong adsorption of water vapor. Since there seems very little probability of accounting for the various decompositions of the esters on the basis of selective adsorption of the reaction products, it is probable that a complete explanation of the phenomena of contact catalysis is not to be found along these lines.

If changes in the chemical potential are not the important factors in contact catalysis, the catalytic agent must change the chemical resistance in some way, and there are two possible ways in which this might happen. We may have more effective collisions between existing molecules or we may have a conversion of one or more of the reacting substances into an active form.

According to the kinetic theory the reaction velocity is pro-

¹ W. C. McC. LEWIS suggests the terms reactants and resultants for reacting substances and reaction products.

² IPATIEFF: *Ber. deutsch. chem. Ges.*, **34**, 3579 (1901); **35**, 1047, 1057, (1902) **36**, 1990, 2003, 2014, 2016 (1903); SABATIER and SENDERENS: *Comptes rendus*, **136**, 738, 921, 936, 983 (1903).

³ JOHNSON: *Jour. Am. Chem. Soc.*, **34**, 911 (1912).

⁴ ENGELDER: *Jour. Phys. Chem.*, **21**, 676 (1917).

portional to the number of collisions between possibly reacting molecules; but it does not follow at all that two molecules react every time they collide. If a large number of collisions is necessary on an average before a pair of molecules react, anything which would make these collisions more helpful might increase the reaction velocity enormously. The first question is then whether there is any evidence of ineffective collisions. This matter has been studied by Strutt¹ who comes to the conclusion that a molecule of ozone reacts every time it strikes a molecule of silver oxide; but that a molecule of active nitrogen collides with a molecule of copper oxide five hundred times on an average before they react, while two molecules of ozone at 100° collide on an average 6×10^{11} times before they react. Without insisting on the absolute accuracy of these figures there is evidently plenty of margin for an increase in reaction velocity with ozone at 100° if one could produce more effective collisions. Langmuir² finds that 15 percent of all oxygen molecules at a pressure of not over 5 bars striking a tungsten filament at 1770°K react with it to form tungstic oxide, WO_3 . This coefficient increases at higher temperatures and at 3300°K about 50 percent of all the oxygen molecules which strike the filament react with it to form WO_3 . Since there are three atoms of oxygen in WO_3 and only two in the oxygen molecule, Langmuir considers that at least one-half of the tungsten surface must be covered at 3300°K with oxygen in some form.

It is possible that a catalytic agent may cause one molecule to strike another amidships instead of head-on and may thereby increase the effectiveness of the collisions. It is not impossible that part at least of the effect of solvents on reaction velocity may be due to some such thing as this. If we adopt Langmuir's views³ of oriented adsorption, all sorts of things become possible. If ethyl acetate, for instance, attaches itself to one adsorbent by the methyl group, to another by the ethyl group, and to a third by the carboxyl group, it might very well be that bombardment of the captive molecule by free ones might lead to very different reaction products in the three cases. Such a suggestion

¹ Proc. Roy. Soc., **87A**, 302 (1912).

² Jour. Am. Chem. Soc., **35**, 105 (1913); **38**, 2270 (1916).

³ Cf. DEBUS: Jour. Chem. Soc., **53**, 327 (1888).

is of very little value, however, unless it can be made definite. We do not know as yet whether ethyl acetate is actually adsorbed in one way by nickel, in another way by thoria, and in a third way by titania, nor do we know whether the difference in the manner of adsorption, assuming it to occur, is of such a nature as to account for the differences in the reaction products. It may well be that some entirely different hypothesis will prove necessary. The general problem of increasing the effectiveness of molecular collisions is distinctly an important one which has not been studied at all.

There is one special case in which we can apparently identify one of the factors of chemical resistance. Buchböck¹ studied the decomposition of carbonyl sulphide and found that the reaction velocity decreased with increasing viscosity of the solution. Since the reaction products are gases, this suggests the possibility that the retardation is due to the greater difficulty of forming gas bubbles in a more viscous medium. This receives confirmation from Raschig's work on the preparation of hydrazine,² by the action of hypochlorite on ammonia, the evolution of nitrogen being kept down by something like starch to make the solution more viscous. The preliminary reaction is $\text{NH}_3 + \text{NaClO} = \text{NH}_2\text{Cl} + \text{NaOH}$ and high viscosity promotes the reaction $\text{NH}_2\text{Cl} + \text{NH}_3 = \text{N}_2\text{H}_4\text{HCl}$ as against the one $3\text{NH}_2\text{Cl} + 2\text{NH}_3 = 3\text{NH}_4\text{Cl} + \text{N}_2$.

Instead of more effective collisions between unchanged portions of the reacting molecules we may have a partial conversion of one or more of the reacting substances into active forms either through the rupture of normal valences or of contra-valences, opening up fields of force as Baly³ puts it.

The conception of Baly that a catalytic agent activates the reacting substances by opening up fields of force covers the ground admirably as a purely formal statement. The trouble with it is that it is as yet too vague to be of any value as a working hypothesis, though it is undoubtedly the best starting-point. It is necessary to show in each particular case just what happens and why it happens. While the conversion of a reacting sub-

¹ *Zeit. phys. Chem.*, **23**, 123 (1897); **34**, 229 (1900).

² HENDERSON: *Catalysis in Industrial Chemistry*, 60 (1919).

³ *Jour. Chem. Soc.*, **101**, 1469, 1475 (1912).

stance into an active form may very well account for the effect of the solvent on reaction velocity in homogeneous systems, it must be shown what active form is produced and why one solvent produces more of it than another. Activation may lead to the formation of intermediate compounds or it may not; but we have got to get down to more definiteness in all the cases of contact catalysis. It is often assumed that definite intermediate compounds are formed and this is certainly true in some cases. In the catalysis of hydrogen peroxide by mercury, the intermediate formation of mercuric peroxide can be detected by the eye because there is an intermittent formation of a film, which then breaks down, only to form again.¹ The formation of graphite is usually preceded by the formation of a carbide. The conversion of acetic acid into acetone² by passing the vapor over heated barium carbonate presumably involves the intermediate formation of barium acetate, though one cannot ear-mark the carbon dioxide and so cannot be absolutely certain that the barium carbonate is continually decomposed and regenerated. In the Deacon chlorine process, where a mixture of hydrochloric acid and oxygen is passed over heated cupric chloride, Hurter³ assumes the existence of an intermediate compound. People are not agreed, however, whether the intermediate compound is cuprous chloride, cupric oxychloride, or both. The extreme sensitiveness of this reaction to poisons raises a question whether an intermediate compound really is formed. In the catalytic oxidation of carbon monoxide, it is usually believed that there is alternate reduction and oxidation of the oxides which act as catalytic agents.

Sabatier⁴ believes that the catalytic action of alumina on alcohol is due to the intermediate formation of an instable compound of alumina and water. On the other hand, Henderson⁵ assumes the intermediate formation of aluminum ethylate. Neither one offers any experimental evidence in support of his

¹ BREDIG and VON ANTROPOFF: *Zeit. Elektrochemie*, **12**, 581 (1906); VON ANTROPOFF: *Jour. prakt. Chem.* (2) **77**, 273 (1908).

² SQUIBB: *Jour. Am. Chem. Soc.*, **17**, 187 (1895).

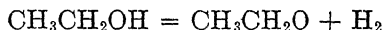
³ *Jour. Soc. Chem. Ind.*, **2**, 106 (1883).

⁴ *Die Katalyse in der organischen Chemie*, 240 (1914).

⁵ *Catalysis in Industrial Chemistry*, 4 (1919).

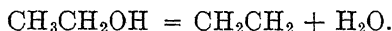
belief, and neither one discusses why kaolin should act practically as well as alumina.

It seems probable that the best way to solve the problem of contact catalysis is to start with the side which has been neglected a good deal and to study the selective action of catalytic agents. Quite apart from any theory we may adopt, there are certain questions which ought to be answered experimentally and yet these questions have not even been raised in a serious way. We know that ethyl alcohol can be decomposed into acetaldehyde and hydrogen or into ethylene and water but that is practically all that we know as yet about these reactions. With pulverulent nickel the reaction is almost completely



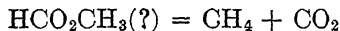
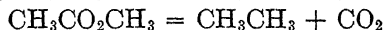
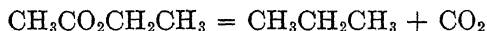
We do not know whether the hydrogen comes off in one stage or in two. If it comes off in two stages, is the first stage $\text{CH}_3\text{CH}_2\text{O}$ or CH_3CHOH ? While it may not be easy to devise a method which will answer this question, the problem is not more difficult than many which the organic chemists have solved successfully.

With pulverulent alumina the reaction is almost completely

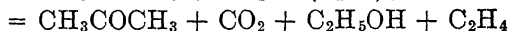


Does water split off as such or do we get the splitting off of hydroxyl or hydrogen? It seems improbable that water can split off as such because then it would be difficult to account for the intermediate formation of ether. If the first stage is a splitting off of hydroxyl does the other hydrogen come from the adjacent carbon atom giving ethylene direct or does it come from the same carbon atom, forming a substituted methylene, CH_3CH , which then rearranges to ethylene? One would also like to know what nickel does with diethyl ether.

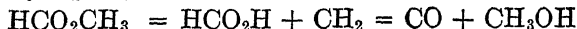
With nickel we get the following decomposition of the esters:



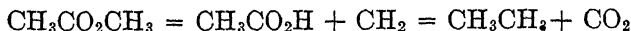
With thorium the decomposition is quite different:



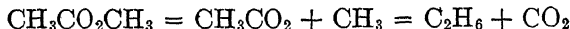
With titania we have a third set of products:



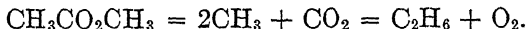
The decompositions are regular and characteristic with each catalytic agent and the molecules must break or slip at different points in the different cases; but we certainly ought to know what the hypothetical intermediate stages are.¹ Take the case of methyl acetate with nickel, for instance. One assumption might be that we have a methylene dissociation



A second assumption is that methyl splits off:



A third assumption might be a splitting off of both methyl groups:



Is any of these what happens and how can we prove it? Also how does the final assumption tie in with the facts that in aqueous solution acetate ion goes to ethane and CO_2



and that dry lead tetra-acetate decomposes at about 140° into lead acetate, methyl acetate and carbon dioxide



The question also comes up as to the changes in the intermediate stages in case the esters are chlorinated more or less completely.

The effect of the catalytic agent is very marked when it comes to the preferential oxidation of mixed gases.² At low temperatures, the nature of the catalytic agent may determine which of two combustible gases will burn the more rapidly. In presence of platinum, copper oxide, or chamotte, hydrogen burns more readily than methane, whereas the reverse is true in borosilicate glass bulbs at 300° – 400° . Depending on conditions, either hydrogen or carbon monoxide will burn the more readily.³

¹ This is now being studied experimentally by PROFESSOR HOMER ADKINS.

² HENRY: *Phil. Mag.*, **65**, 269 (1825); BONE: *Jour. Chem. Soc.*, **81**, 535 (1902); **85**, 694 (1894); *Proc. Roy. Inst.*, **19**, 82 (1908); *Phil. Trans.*, **215**, 298 (1915).

³ RIDEAL: *Jour. Chem. Soc.*, **115**, 993 (1919).

At very high temperatures the specific effect of the catalytic agent becomes negligible because the reaction will take place so rapidly in the gas phase.

One very striking characteristic of solid catalytic agents is the ease with which they become inactive or are poisoned. Since the reaction takes place in or at the surface, it follows that any substance which cuts down the rate at which the reacting substances reach the catalytic surface¹ or which prevents them from reaching it, will decrease the reaction velocity and may destroy the catalytic action entirely. Berliner² has shown that traces of fatty vapors from the air or from the grease on the stop-cocks will decrease the adsorption of hydrogen by palladium from nearly nine hundred volumes practically to nothing. Faraday³ has shown that traces of grease destroy the catalytic action of platinum on oxyhydrogen gas. De Hemptinne⁴ has apparently shown that carbon monoxide cuts down the adsorption of hydrogen by palladium, though his method of presenting his results is very obscure. Lunge and Harbeck⁵ found that carbon monoxide inhibits practically completely the catalytic action of platinum on a mixture of ethylene and hydrogen. Schönbein⁶ pointed out that the hydrides of sulphur, tellurium, selenium, phosphorus, arsenic, and antimony act very energetically in cutting down the catalytic action of platinum on mixtures of air with hydrogen or ether. He considered that the hydride must decompose, giving rise to a solid film. This is not necessary in order to account for the phenomenon; but he seems to have been right in at least one case, for Maxted⁷ has found that hydrogen sulphide is decomposed by platinum black with evolution of hydrogen and that the platinum then does not adsorb hydrogen. Langmuir⁸ believes that oxygen prevents the dissociation of hydrogen by a heated tungsten filament because it cuts down the adsorption of the hydrogen.

¹ TAYLOR: *Trans. Am. Electrochem. Soc.*, **36** (1919).

² *Wied. Ann.*, **35**, 903 (1888).

³ *Experimental Researches on Electricity*, **1**, 185 (1839).

⁴ *Zeit. phys. Chem.*, **27**, 249 (1898).

⁵ *Zeit. anorg. Chem.*, **16**, 50 (1898).

⁶ *Jour. prakt. Chem.*, **29**, 238 (1843).

⁷ *Jour. Chem. Soc.*, **115**, 1050 (1919).

⁸ *Jour. Am. Chem. Soc.*, **38**, 2272 (1916).

Harned¹ has shown that the rate of adsorption² of chloropierin by a charcoal which has been cleaned by washing with chloropierin is much greater at first than by a charcoal which has not been so cleaned, although the final equilibrium is apparently about the same in the two cases. This is analogous to the evaporation of water when covered by an oil film. The oil cuts down the rate of evaporation very much but has practically no effect on the partial pressure of water at equilibrium. Taylor points out that normally the time of contact between a gas and the solid catalytic agent is extremely small and consequently anything which decreases the rate of adsorption will cut down the reaction velocity very much.

It is easy to see that the piling up of reaction products³ will cut down the reaction velocity, if they prevent the reacting substances from coming in contact with the catalytic agent. This has been observed in the contact sulphuric acid process.⁴ The explanation that the decrease in the reaction velocity is due to a decreased adsorption of the reacting substances was first given by Fink⁵ who is the real pioneer in this line. Although the reaction between carbon monoxide and oxygen is practically irreversible at ordinary temperature, Henry⁶ recognized that the presence of the reaction product might slow up the rate of reaction and he proved his point by increasing the reaction velocity when he removed the carbon dioxide with caustic potash. Water vapor checks the catalytic dehydration of ether⁷ and of alcohol⁸ and hydrogen cuts down the catalytic dehydrogenation of alcohol.

When catalytic poisons are present or are formed during the reaction, the apparent equilibrium may vary with the amount of the catalytic agent. With only a small amount present, the catalytic agent will be poisoned before the reaction has run very far. In the hydrolysis of ethyl butyrate by enzymes, the reaction

¹ Jour. Am. Chem. Soc., **42**, 372 (1920).

² TAYLOR: Trans. Am. Electrochem. Soc., **36** (1919).

³ BUNSEN (1857). Quoted by DEACON: Jour. Chem. Soc., **23**, 736 (1872).

⁴ BODLÄNDER and KOPPEN: Zeit. Elektrochemie, **9**, 566 (1903); BERL: Zeit. anorg. Chem., **44**, 267 (1905).

⁵ BODENSTEIN and FINK: Zeit. phys. Chem., **60**, 61 (1907).

⁶ Phil. Mag. (3) **9**, 324 (1836).

⁷ IPATIEFF: Ber. deutsch. chem. Ges., **37**, 2996 (1904).

⁸ ENGELDER: Jour. Phys. Chem., **21**, 676 (1917).

apparently runs to different end-points, depending on the relative amounts of enzyme.¹ One may also get abnormal end-points in the hydrolysis of a solid, if the product of hydrolysis is also a solid and forms a film over the reacting substance. With one of the war gases, the amount of hydrochloric acid split off in presence of water was practically the same when the amount of water added varied in the ratio of one to four. In other words, an apparent equilibrium was reached at a given concentration of hydrochloric acid in one case and at one-fourth that concentration when four times as much water was added.

The development of some of the technical contact processes has been so interesting that it seems worth while to discuss a few of them briefly, beginning with the contact sulphuric acid process.²

CONTACT SULPHURIC ACID PROCESS

In 1831 Phillips discovered that spongy platinum increases the rate at which sulphur dioxide combines with oxygen according to the equation $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$. He obtained a patent for this but could not develop a commercial process. In 1846 Jullion patented the use of platinized asbestos. In 1842 Wöhler and Mahla discovered that the oxides of copper, iron, and chromium act like platinum. In the Schroeder-Grillo contact material hydrated magnesium sulphate is soaked in a solution of a platinum salt and then heated in presence of sulphur dioxide. A thin layer of platinum is thus precipitated on the surface of the porous, dehydrated salt, 0.2-0.3 percent of platinum giving an excellent catalytic agent.³

Knietsch found that a practically complete conversion of sulphur dioxide into sulphur trioxide could be obtained when sulphur dioxide was diluted with air, the conversion being more nearly complete the greater the ratio of oxygen to sulphur dioxide.

When the experiments were repeated with purified burner gas on a commercial scale, the contact material soon became inert. It was found that this disastrous result was due to impurities in the burner gases. Even when present in apparently negligible

¹ KASTLE and LOEVENHART: *Am. Chem. Jour.*, **24**, 491 (1900).

² KNIETSCH: *Ber. deutsch. chem. Ges.*, **34**, 4069 (1901).

³ RIDEAL and TAYLOR: *Catalysis in Theory and Practice*, 86 (1919).

amounts, these impurities play havoc with the catalytic action of the platinum. Arsenic is the most dangerous and next mercury, while antimony, bismuth, lead, iron, zinc, etc., act in so far as they settle on and actually blanket the contact material. An amount of arsenic equal to 1-2 percent of the platinum in the contact material will destroy the catalytic action completely. In view of the enormous volumes of gas which are handled, it is easy to see to what an infinitesimal value the arsenic content must be reduced.

By cooling the burner gases slowly and bringing them into intimate contact with sulphuric acid, it was found possible to obtain a gas mixture which passed all ordinary optical and chemical tests and which appeared to be pure. When tested on the large scale, it was still found to contain arsenic. The gases had been cooled in long iron tubes and had reacted with these sufficiently to give traces of arsine. This difficulty was eliminated by not letting the gases come in contact with the iron. When the roaster furnaces were run to maximum capacity, however, a slight cloud was formed which could not be got rid of and which proved to consist of unburned sulphur. This in itself would have done no harm had not the particles of sulphur contained some arsenic. It therefore proved necessary to admit enough air so as to be sure that the sulphur was burned completely. While no one has shown that the presence of arsenic cuts down the adsorption by platinum, it is quite certain from Berliner's experiments on palladium and hydrogen¹ that this must be the case.

In American practice the burner gases carry arsenic, lead sulphate, silicon tetrafluoride, hydrochloric acid, sulphur, and selenium. Reese² calls the first two permanent poisons and the others temporary poisons. When working with platinum on a magnesium sulphate base, it is possible to regenerate the contact material after it has been poisoned with arsenic by heating with hydrochloric acid. The assumption was that the arsenic was volatilized as the trichloride. Analysis showed, however, that there might be 2-3 percent of arsenic in the regenerated catalyst without its having any apparent effect. It must be that the

¹ BERLINER: Wied. Ann., **35**, 804 (1888).

² Jour. Soc. Chem. Ind., **22**, 351 (1903).

arsenic had agglomerated in some way so that it did not coat the platinum. In spite of Knietzsch's statement to the contrary, it is possible to filter out all the solid poisons.

Under ordinary conditions sulphur dioxide and oxygen combine very slowly and sulphur trioxide dissociates very slowly in the absence of catalytic agents. In presence of catalytic agents sulphur trioxide begins to dissociate perceptibly at about 400° and is practically completely dissociated at 1000°. At first sight it would therefore seem that the process should be run below 400°. The time factor is a complicating one, however. With platinum as catalytic agent the reaction begins at about 200°, but is relatively slow at that temperature, and under commercial conditions there is practically no reaction below 400°. It has proved best technically to work at about 425°–450°, the increased reaction velocity compensating for the decreased chemical efficiency. At 425° the conversion is 98 percent, dropping to 91 percent at 500°. Ferric oxide can be used as a catalytic agent; but the reaction velocity is less and consequently it is necessary to work at a higher temperature with a correspondingly lower chemical efficiency, perhaps 60 percent. Ferric oxide is much less susceptible to arsenic poisoning than is platinum, presumably because of the higher temperature at which it acts. Since arsenic oxide is itself a catalytic agent when free from iron,¹ there must be temperatures at which it will have little or no deleterious action. If one could make a ferric oxide catalyst which would work at as low a temperature as platinum, it is probable that it would be about as sensitive to arsenic poisoning as platinum. It is entirely a question of the way in which the arsenic precipitates on the surface of the catalytic agent.

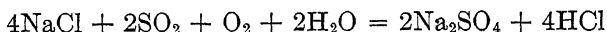
The heat of reaction for the conversion of sulphur dioxide into sulphur trioxide is given as 22,600 cal per mol of gaseous sulphur trioxide. Since this heat is evolved at the surface of the contact material, it is quite a serious matter to keep the temperature within the proper range. The technical manufacture of sulphur trioxide is therefore very largely an engineering problem and the recent improvements have been chiefly changes in design² so as to give more efficient temperature control.

¹ Cf. BERL: *Zeit. anorg. Chem.*, **44**, 267 (1905).

² ZEISBERG: *Trans. Am. Electrochem. Soc.*, **36** (1919).

HARGREAVES SALT-CAKE PROCESS

The Hargreaves and Robinson process¹ for making salt-cake was established on a practical basis in 1870. The upper temperature limit is about 600° owing to the fusion of the salt. Originally the process involved no catalytic agent but consisted simply in the passage of pyrites gases over suitably prepared salt at 500°–550°, the reaction being



In 1886 small amounts of iron oxide were added as a catalytic agent. Krutwig² showed that without ferric oxide about 28 percent of the sulphur in pyrites was converted into sodium sulphate after four hours at a red heat. With ferric oxide a 70 percent yield was obtained at high temperatures and 90 percent at lower ones. The action is also accelerated by cupric oxide and, since 1907, 0.1–1.0 percent of copper or iron salts or both have been added to the salt before the latter is moulded, the amount added depending on the required purity of the product. When the salt-cake is to be used in glass works, only a small amount of the catalytic agent can be added; but the maximum amount is permissible when the salt-cake is intended for the LeBlanc soda process. Increasing the amount of catalytic agent increases the reaction velocity and lowers the temperature at which the action starts. In this particular process there is little or no difficulty with the poisoning of the catalytic agent because the oxides are not used over and over again.

DEACON CHLORINE PROCESS

In 1845 Oxland³ discovered that chlorine is formed to some extent when a mixture of hydrochloric acid and oxygen is passed over a heated porous substance. The reaction is $4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Cl}_2$; but the reaction does not proceed fast enough to be

¹ THORPE: Dictionary of Applied Chemistry, 5, 25 (1913); JOBLING: Catalysis and its Industrial Applications, 32 (1916); RIDEAL and TAYLOR: Catalysis in Theory and Practice, 89 (1919).

² Recueil Trav. chim. Pays-Bas, 16, 173 (1897).

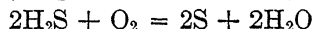
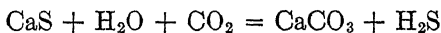
³ THORPE: Dictionary of Applied Chemistry, 2, 18 (1918); JOBLING: Catalysis and its Industrial Applications, 26 (1916); RIDEAL and TAYLOR: Catalysis in Theory and Practice, 99 (1919).

ADSORPTION OF GAS OR VAPOR BY SOLID

practicable commercially. In 1855 Vogel treated cupric chloride alternately with hydrochloric acid and oxygen. In 1888 Deacon and Hurter put the process on a successful technical basis by passing a mixture of hydrochloric acid and oxygen over pumice impregnated with cupric chloride which acts as a catalytic agent. It is usually assumed that this is not a case of adsorption catalysis but that the cupric chloride breaks up into chlorine and cuprous chloride which latter combines with oxygen to form cupric oxychloride, $\text{CuO} \cdot \text{CuCl}_2$. This reacts with hydrochloric acid to form cupric chloride, after which the whole series of reactions take place again and again. There is no real proof of this¹ and it is really quite as probable that the oxygen does react direct with the hydrochloric acid, which is what it must do when there is no cupric chloride present. The catalytic agent is very sensitive to the effect of impurities, such as sulphur dioxide, sulphur trioxide, and arsenic. It is because of this sensitiveness to sulphur dioxide that the hydrochloric acid from the Hargreaves salt-cake process cannot be used in the Deacon process. Water is also bad for the reaction. The gases are therefore dried at 40° before entering the decomposer, as it is called. The temperature at which the best results are obtained is about 450° – 460° . Above this temperature the cupric chloride volatilizes too rapidly and at lower temperatures the reaction velocity is too low. About two-thirds of the hydrochloric acid is converted into chlorine.

CHANCE-CLAUS PROCESS

In the LeBlanc process for making sodium carbonate, calcium sulphide is a by-product. As far back as 1837 Gossage² patented a process for using this tank waste. His plan was to treat the calcium sulphide with carbon dioxide and then to burn the resulting hydrogen sulphide to sulphur according to the equations,



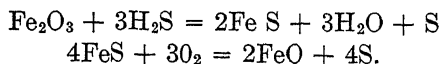
Gossage failed because he could not get a sufficiently concentrated CO_2 to start with or a sufficiently concentrated hydrogen sulphide for the second stage of the process. This problem was solved by Chance in 1887.

¹ HURTER: Jour. Soc. Chem. Ind. **2**, 106 (1883).

² JOBLING: Catalysis and its Industrial Applications, 33 (1916).

The burning of the hydrogen sulphide was carried out according to a process patented by Claus but developed further by Chance.¹ The Claus kiln consists of a cylinder provided internally with a grating upon which rests a layer of broken fire-brick, with a further layer of bog-iron ore superimposed. The combustible mixture enters at the top, passes through the porous layers, where it is burned to sulphur vapor and steam with but little sulphur dioxide and sulphuretted hydrogen as impurity, and is drawn from the bottom into a series of condensing chambers, where part of the sulphur vapor condenses to liquid sulphur and the remainder as flowers of sulphur along with the condensed steam. The reaction is exothermic, so that no external heating is necessary. To start the reaction, a few shovelfuls of red-hot coal are thrown on to the oxide; whilst the temperature is regulated by controlling the speed of the gas. During the process the ferric oxide becomes transformed into pyrites, but the pyrites so formed has some peculiar property attached to it which ordinary pyrites do not possess, for the latter is quite useless as a catalyst. When once the necessary temperature has been reached, the reaction is found to proceed fairly satisfactorily with other contact material such as broken brick, though the working temperature then becomes somewhat higher than when ferric oxide only is employed. For starting the reaction, however, ferric oxide or similar contact material must be employed; hence the two layers in the Claus kiln.

Salamon² says that the ferric oxide undergoes no change. If that is so, it is not necessary to account for the difference in behavior between natural pyrites and that formed in the Claus kiln. If iron sulphide is actually formed, the alleged difference in behavior is undoubtedly due to a difference in surface and consequently of adsorption. The natural pyrites is of course only very slightly porous. Rideal and Taylor³ consider that the reaction takes place in two stages,



They do not discuss the behavior of natural pyrites.

¹ JOBLING: *Catalysis and its Industrial Applications*, 33, (1916).

² THORPE: *Dictionary of Applied Chemistry*, 5, 294 (1917).

³ *Catalysis in Theory and Practice*, 112 (1919).

ADSORPTION OF GAS OR VAPOR BY SOLID

HABER AMMONIA PROCESS

In the contact sulphuric acid process it was found that sulphur trioxide dissociates practically completely into sulphur dioxide and oxygen, at 1000° , while recombination is practically complete at 400° if equilibrium is reached. Matters are not so favorable in the case of the synthesis of ammonia from nitrogen and hydrogen. At 1000° ammonia is practically completely dissociated just as is sulphur trioxide; but at 550° the theoretical amount of recombination at atmospheric pressure is about 0.08 percent instead of 100 percent. Increase of pressure displaces the equilibrium so that more is formed of the system occupying the lesser volume, namely ammonia. At 550° and 200 atm. the amount of ammonia formed is almost 12 percent. The data¹ are given in Table XVIII.

TABLE XVIII.—EQUILIBRIUM DATA FOR AMMONIA SYNTHESIS

Reaction is $N_2 + 3H_2 = 2NH_3$

Pressure in atm.	550°	650°	750°	850°	1000°
	Percentage ammonia				
1	0.077	0.032	0.916	0.008	0.006
10	0.7	3.02	1.54	0.87	0.54
200	11.9	5.71	2.99	1.68	1.07

Though the yield of 12 percent is low, the ammonia can be removed as ammonia of crystallization by ammonium nitrate at low temperatures,² a fresh supply of the reacting gases can be added to the unchanged nitrogen and hydrogen, and the whole can be passed repeatedly through the reacting chamber until the concentration of methane and argon becomes too high.³ What catalytic agent to use is a question of first importance. The first catalytic agents tried were nickel, manganese, iron and chromium; afterwards experiments were made with osmium and

¹ HABER: Jour. Soc. Chem. Ind., **33**, 53 (1914).

² THORPE: Outlines of Industrial Chemistry, 151 (1916).

³ RIDEAL and TAYLOR: Catalysis in Theory and Practice, 241 (1919).

uranium.¹ While metallic osmium and uranium carbide are apparently the best for laboratory work, they are not well adapted for technical use.² Judging by the most recent patents, pure iron³ is the catalyst generally employed in this process. Using this material and with the aid of various minor improvements, it is said to be found possible to lower the working pressure to the neighborhood of 50 atmospheres. In all cases, it is essential in the interests of efficiency, that the catalyst be prepared at a temperature not greatly exceeding 600°. Of the remaining substances which catalyze the reaction, the most interesting are molybdenum and molybdates, tungsten and its alloys, and cerium with its congeners. Platinum, on the other hand, though related to osmium, possesses but a slight catalytic activity. It was found that the activity of the catalysts can be increased by the addition of certain foreign bodies. These "promoters," as they have been called, include various metals, the oxides, hydroxides, and salts of the alkali and alkaline earth metals, as well as many other substances of the most varied nature. In many cases just a trace of the contaminating body enhances considerably the activity of the catalyst. Moreover, all the catalysts appear to possess the capacity for invigoration.⁴ There are no data to show whether these so-called promoters change the degree of adsorption of any of the substances concerned in the reaction or whether they prevent a possible sintering of the catalytic agent. Mannich and Thiel⁵ state that charcoal increases the adsorbing power of palladium for hydrogen. Rideal and Taylor⁶ consider that the promoters may cause the relative adsorption of the reacting substances to approach the theoretical ratios more closely.

The contact ammonia process is very susceptible to poisons. Among the harmful substances are sulphur, selenium, tellurium, phosphorus, arsenic, boron, and their compounds; many carbon compounds; lead, zinc, bismuth, tin, etc.⁷ Such minute quanti-

¹ HABER: *Jour. Soc. Chem. Ind.*, **33**, 54 (1914).

² JOBLING: *Catalysis and its Industrial Applications*, 42 (1916).

³ Cf. JELLINEK: *Zeit. anorg. Chem.*, **71**, 121 (1911).

⁴ PEASE and TAYLOR: *Jour. Phys. Chem.*, **24**, 241 (1920).

⁵ *Jour. Soc. Chem. Ind.*, **35**, 548 (1916).

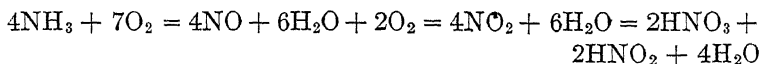
⁶ *Catalysis in Theory and Practice*, 29 (1919).

⁷ JOBLING: *Catalysis and its Industrial Applications*, 44 (1916).

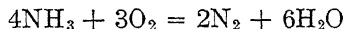
ties of any of the above-mentioned substances as are to be found almost always in the purest commercial products and so-called pure gases are sufficient to diminish the catalytic efficiency very seriously. For instance, an impurity of 0.01 percent sulphur in iron renders it nearly useless. The Haber process was of enormous value to the Germans during the war.

OSTWALD NITRIC ACID PROCESS

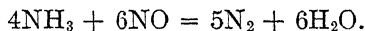
In 1830 Kugelman¹ observed that ammonia can be oxidized to nitric acid in presence of platinum. About eighty years later the process was put on a semi-commercial basis by Ostwald. The nominal reaction may be written $\text{NH}_3 + 2\text{O}_2 = \text{HNO}_3 + \text{H}_2\text{O}$; but the real reaction is the formation of nitric oxide, which is then oxidized to nitrogen peroxide, and afterwards converted into nitric acid,



The problem is complicated by the apparently simultaneous oxidation to nitrogen, a reaction which is usually written



It is more likely that the disturbing reaction is an oxidation of ammonia by nitric oxide,² perhaps



Both the reactions are accelerated by platinum; but, fortunately, the reaction yielding nitric oxide takes place much more rapidly than the reaction giving rise to nitrogen. The best results are obtained by keeping the gases in contact with the catalytic agent for as short a time as possible, which is an argument for the reaction producing nitrogen being a secondary one. If the two reactions took place simultaneously, the ratio of the two sets of products should be independent of the rate of passage of the gaseous mixture. A mixture of ammonia with ten or more volumes of air is passed at a velocity of 1-5 meters per second

¹ JOBLING: *Catalysis and its Industrial Applications*, 45 (1916).

² SABATIER and SENDERENS: *Comptes rendus*, **135**, 278 (1902).

through a plug of platinum gauze, 1-2 cm in length and kept at 300°. This gives a period of contact not exceeding 0.01 sec. Under favorable conditions an 85 percent conversion of ammonia is claimed. Better results have been obtained in this country,¹ with several layers of platinum gauze,² the yield running 92 percent, with a flow of 250 cubic feet per minute. The average concentration of ammonia is 10.7 percent. A smooth platinum gauze is not effective. After some time it becomes roughened and activated. Contrary to what Ostwald had believed, a high temperature, say above 825°, is better than a lower one. Phosphine is a bad poison, having a distinct effect even when present three parts per hundred million, but cyanogen compounds are not bad because they oxidize readily. Iron oxide, grease, oil or tar must be kept away from the platinum gauze and a new gauze should be washed with pure gasoline or ether before being activated. Ammonia from any source can be used though Landis³ claims that the platinum must be activated anew when changing to a different ammonia.

SABATIER'S HYDROGENATION PROCESS

Sabatier and Senderens⁴ discovered, a number of years ago, that reduced nickel will cause hydrogen to combine with ethylene or acetylene forming ethane. This has since developed into a general hydrogenation process.⁵ The principle of the method is a simple one. The vapor of the substance to be reduced is mixed with hydrogen and passed directly over specific metallic catalysts maintained at temperatures usually held between 150° and 300°. The process is extremely rapid, since complete hydrogenation occurs during the short time the mixture is passing over the catalyst. Rapidity, however, is not the only advantage, for Sabatier and his collaborators, Senderens, Mailhe, and others, who have worked on this method for some fifteen years, find it to be one which, whilst requiring the minimum of attention, furnishes very high yields.

¹ PARSONS: *Jour. Ind. Eng. Chem.* **11**, 541 (1919).

² PERLEY: *Jour. Ind. Eng. Chem.* **12**, 5, 119 (1920).

³ *Trans. Am. Electrochem. Soc.*, **35**, 300 (1919).

⁴ *Comptes rendus*, **124**, 1358 (1897); **128**, 1173 (1899).

⁵ JOBLING: *Catalysis and its Industrial Applications*, 68 (1916); SABATIER: *Die Katalyse in der organischen Chemie*, 44 (1914).

The metals which are suitable as catalysts are nickel, cobalt, platinum, iron and copper, of which nickel is far and away the most active, while the others are arranged in diminishing activity. As would be anticipated, the practicability of the method depends largely upon the condition in which the metal is used. It must be prepared by reduction of the oxide, the activity depending upon the nature of the oxide employed and the temperature at which it is reduced. In general the greater the surface exposed the greater the activity, so that the conditions must be carefully arranged to satisfy this requirement. Reduction at a low temperature is found to yield a metal which is too active and too sensitive to external influences, while reduction at a high temperature reduces the catalytic action almost to zero. Consequently, a suitable intermediate temperature must be chosen. Sabatier finds that the best nickel for the purpose is produced by dissolving the metal in nitric acid, calcining the nitrate at a dull red heat, and then reducing the oxide slowly at a temperature of about 300°-325°, until water is no longer evolved. After the nickel has been prepared as described, it is necessary to keep it out of contact with the air, as it is extremely pyrophoric and quickly loses its activity on exposure.

Weight for weight, the efficiency of pure nickel is not so great as that which has had its active surface increased by the aid of some suitable carrier. Hence many proposals have been made for combining the catalyst with a great variety of supporting bodies, ranging from pumice and kieselguhr to charcoal and sawdust.

The materials used, whether hydrogen, metal, or organic compound, must be as pure as can be obtained, for any impurity is readily adsorbed by the catalyst to the detriment of its activity. Sulphur and its volatile compounds, as well as the halogens,¹ are particularly to be avoided in this respect, and, to a lesser degree, arsenic and phosphorus with their volatile compounds. Electrolytic hydrogen, or hydrogen of equivalent purity, appears to be essential. Even then the catalyst must, sooner or later, succumb to the toxic effects of minute impurities impossible to remove; in consequence, the desirability of frequent renewals needs emphasis.

¹ The nickel oxide must not be prepared from the chloride because of the great difficulty of washing out the last traces of absorbed chloride.

Of practical importance is the preparation of numerous artificial perfumes by the aid of this reaction. Moreover, it permits of the production of cyclohexanol and *p*-methyl cyclohexanol, easily obtained from phenol and *p*-cresol respectively, which are used in the manufacture of isoprene and butadiene, and seem, therefore, destined to play an important part in the synthesis of rubber.

Probably the most important technical application of Sabatier's hydrogenation process is to the conversion of liquid and unsaturated fatty acids such as oleic acid¹ into solid and saturated acids such as stearic acid. As the acid is not vaporized, this process does not belong strictly speaking under the general head of gas reactions accelerated by solid catalytic agents, so I merely refer to it because it is a further development of the same principle.

SABATIER'S DEHYDROGENATION PROCESS

Attention has already been drawn to the fact that alcohols may split off hydrogen or water at a given temperature, depending on the nature of the catalytic agent. Finely divided metals,² such as copper, cobalt, nickel, iron, platinum, and palladium catalyze almost exclusively the dehydrogenation process. So also do some anhydrous oxides, chief among which are the lower oxides of manganese, tin, uranium, molybdenum, vanadium, and cadmium, though the activity of these is less than that of the metals. The dehydrogenation of alcohols, both primary and secondary, is most readily effected by reduced copper. If a fatty alcohol be passed over this catalyst at 200°–300°, a yield of at least 50 percent aldehyde or ketone can usually be condensed.

Cyclic alcohols may be dehydrogenated in a similar way. Borneol, for instance, can be transformed into camphor by passage over reduced copper at 150°, whilst geraniol under similar conditions gives citral. The former fact is utilized industrially in the treatment of certain camphors which are sold very cheaply

¹ Cf. ELLIS: Jour. Soc. Chem. Ind., **31**, 1155 (1912); SHAW: Ibid., **33**, 771 (1914); ELLIS: Jour. Ind. Eng. Chem., **8**, 886 (1916); ELLIS: The Hydrogenation of Oils, 2nd Ed., 108 (1918).

² JOBLING: Catalysis and its Industrial Applications, 82 (1916).

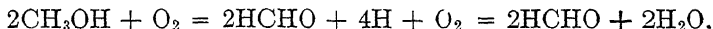
ADSORPTION OF GAS OR VAPOR BY SOLID

on account of their large content of borneol. As the usual process for removing borneol by means of nitric acid is very slow and unsatisfactory, the above dehydrogenation method, which yields nearly pure camphor, has found ready application in this field.

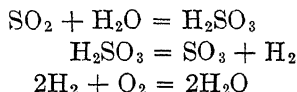
Of the other catalysts, cobalt, iron, platinum, as well as the above-mentioned oxides, are less advantageous. Zinc is stated to possess high activity. Nickel is ruled out on account of the violence of its reaction, for it pushes decomposition too far.

The most important of the industrial applications of this reaction is the preparation of formaldehyde from methyl alcohol.¹ The earliest recorded production of formaldehyde is to be found in the classic experiment of Hofmann's (1867), in which a red-hot coil of platinum wire suspended over methyl alcohol in a beaker continued to glow there so long as it is in contact with a mixture of the vapor and air. This method forms the basis of most of the subsequent attempts and of the present commercial process. Air is driven through wood spirit kept at a temperature suitable for saturation and the mixture then passed into the catalyzer, usually copper gauze.

In the so-called oxidation of methyl alcohol, the primary reaction is the splitting-off of hydrogen² and the practically simultaneous depolarization by oxygen,



Hofmann³ found that osmium tetroxide oxidizes alcohol to aldehyde but not to acetic acid, acting apparently as a carrier for oxygen. It is probable that we have here a catalytic splitting of the alcohol, the nascent hydrogen reacting with the osmium tetroxide. Wieland⁴ considers that the contact sulphuric acid process really involves a dehydrogenation, the reactions being:



¹ THORPE: Dictionary of Applied Chemistry, **2**, 592 (1912).

² LEBLANC and PLASCHKE: Zert. Elektrochemie, **17**, 47 (1911).

³ Ber. deutsch. chem. Ges. **46**, 1657, 2854 (1913).

⁴ Ibid. **45**, 685 (1912).

SURFACE COMBUSTION

The subject of surface combustion has been developed by Bone in England¹ and by Lucke in America. Bone began by a study of the combination of hydrogen and oxygen in contact with hot surfaces of porcelain, magnesia, silver, gold, platinum, nickel, calcined spathic iron ore (containing 79.0 percent ferric oxide and 14.5 percent manganous oxide), nickelous oxide, and copper oxide. With each of these surfaces the rate is proportional to the pressure of the dry gas when electrolytic gas is used, is approximately proportional to the partial pressure of hydrogen when either gas is present in excess, and is increased by a previous treatment with hydrogen. In the case of porcelain, Bone decides that porous porcelain occludes or condenses both hydrogen and oxygen at rates which depend to some extent upon the physical condition and past history of the surface. While the process is extremely rapid in the case of oxygen and the surface layer is soon saturated, the occlusion of hydrogen is slower and the limit of saturation much higher. Combination between the occluded gases occurs at a rate either comparable with, or somewhat faster than, the rate at which the film of occluded oxygen is renewed, but considerably faster than the rate of occlusion of hydrogen.

In later papers Bone² showed that all incandescent substances are capable of accelerating gaseous combustion; and to an approximately equal degree, for the wide differences between the catalytic powers of various surfaces at low temperatures gradually diminish as the temperature rises, until at incandescence they practically disappear. If an explosive mixture of a combustible gas and air is pressed through the pores of a granular, high-melting solid, and if the issuing gas be lighted, it will speedily raise the granular solid to incandescence if the conditions are right, after which the heated surface will accelerate the rate of combustion so much that the whole of the gas will be burned at the surface of the solid and we shall have what has been called flameless combustion. As a matter of fact there is flame, but the flame is so short and the light from the incandescent solid so intense that there seems to be no flame. The combustion

¹ Phil. Trans., **206A**, 1 (1906); Jour. Franklin Inst., **173**, 101 (1912).

² Summarized in Ber. deutsch. chem. Ges., **46**, 5 (1913); JOBLING: Catalysis and its Industrial Applications, 51 (1916).

takes place only at the surface layer of the granular solid but all over the surface and not as flames between each solid particle. The advantages of this surface combustion are an intense and a localized heat, combustion with minimum excess of air, and the development of a large amount of the heat as radiant energy. By passing the explosive mixture through a porous diaphragm we get an incandescent surface which can, if need be, be held glowing side down over a solution which is to be evaporated. In this way, it is possible, for instance, to evaporate a water-glass solution without danger of bumping. The sodium silicate forms as a solid film on the surface of the solution and can be removed from time to time. This form of heating has proved very successful in making candy.¹

The granular mass may be piled in round a crucible or around boiler tubes giving an extremely high efficiency. The maximum temperature depends on the working conditions. The choice of refractory material is determined by the temperatures involved. Under ordinary conditions calcined fire-clay, ganister, etc., are used; but when high temperatures are in question, practically all solids are eliminated except calcined magnesia and carborundum. Attempts are now being made to substitute an atomized liquid fuel for a gaseous fuel. It is stated that the most successful applications of surface combustion to large scale work are where the heat is radiated very quickly so that the temperature of the refractory does not rise unduly—with steam boiler tubes packed in refractory material for instance.² Surface combustion furnaces have proved very useful in annealing shell.

Since an explosive gas mixture is used, it is necessary to keep the flame from working back and burning in the mass of the refractory instead of on the surface. Bone does this by regulating the rate of flow of the gaseous mixture. Lucke³ has described several ways of doing this by special construction of the heater.

WELSBACH GAS MANTLE

The invention of the gas mantle made it possible for gas to continue to compete with electricity as an illuminant. The

¹ SEAGER: *Jour. Franklin Inst.*, **177**, 367 (1914).

² Reports of Progress of Applied Chemistry, **1917**, 26.

³ *Jour. Ind. Eng. Chem.*, **5**, 801 (1913).

best results are obtained when the Welsbach gas mantle consists of 99 percent thoria and 1 percent ceria.¹ Pure thoria gives a relatively poor light, but the continuous addition of ceria gradually increases the luminosity to a maximum of ten-fold when 1 percent is present. Any further addition then diminishes the luminosity until, with 10 percent the difference in effect is unappreciable. In present-day manufacture, the cotton, silk or ramie web is impregnated with a 25-33 percent aqueous solution of thorium and cerium nitrates in the proportion of 99:1, together with a little hardening medium, *e.g.*, beryllium nitrate, if necessary.

We are dealing with surface combustion both in the case of the lime light and of the Welsbach mantle, as is shown by the rapid decay of the light of the lime light owing to sintering² and the similar though much slower decay of the light of the Welsbach mantle. Mantles of magnesia and lanthana give a good light when new; but the light decreases as the surface becomes glassy. While a thoria mantle reaches a high temperature,³ its emissive power is low. Ceria has a high emissive power in the visible spectrum; but the energy of radiation is so great that the temperature of a ceria mantle does not rise high enough. Starting with thoria and increasing the amount of ceria increases the emissive power but lowers the temperature of the mantle. The maximum luminous efficiency is obtained when the rise of visible emission due to the ceria is balanced by the drop in the temperature of the mantle due to the increased radiation. The ceria may form a solid solution with the thoria but there seem to be no data to show whether equilibrium is actually reached in the mantle.

¹ JOBLING: Catalysis and its Industrial Applications, 62 (1916).

² STEINMETZ: Radiation, Light and Illumination, 92 (1909).

³ IVES, KINGBURY and KARRER: Jour. Franklin Inst., 186, 401, 585 (1918).

CHAPTER II

ADSORPTION OF VAPOR BY LIQUID AND OF LIQUID AND SOLID BY SOLID AND LIQUID

ADSORPTION OF VAPOR BY LIQUID

Campbell¹ believes that one source of error in the method of determining molecular weights by the so-called air-bubbling method is due to the formation of a film of adsorbed air on the surface of the solution which interferes with the evaporation. He deduced the existence of an adsorbed gas film from his quantitative measurements on evaporation. The existence of such a film is shown directly by Rayleigh's experiments on liquid jets.² A vertical jet of water or any liquid slows up and breaks into drops when the head is sufficiently great relatively to the diameter of the jet. These drops scatter because they rebound when they strike one another. If a feebly electrified body is brought close to the jet, the jet becomes coherent. Under more powerful electrical action the scattering of the drops becomes even greater than when there is no electrification. What happens is that there is formed round each drop a film of adsorbed air which prevents two drops from coalescing when they collide. When the drops are electrified, the air film is removed to such an extent that the drops come more nearly in contact and coalesce. With higher electrification, a marked charging of the drops takes place and the repulsion of the like charges causes the drops to scatter. Nipher³ states that drops of 1 mm radius do not attract each other when charged to 0.0031 volt. That there is an air film between the drops can also be shown by letting two jets impinge under such conditions that they bound apart. It was found that whenever the jets rebounded, the electrical insulation was practically perfect. Rayleigh found that presence of dust

¹ Trans. Faraday Soc., **10**, 197 (1915).

² RAYLEIGH: Proc. Roy. Soc., **28**, 406; **29**, 71 (1879); **34**, 130 (1882).

³ Science, **34**, 442 (1911).

or addition of a drop of milk had a marked effect on the ease with which the drops coalesce. The reason for this has not been worked out.

In Worthington's experiments on splashes¹ the adsorbed air film plays an important part. A drop of water may fall on a sheet of water in such a way that the drop passes below the surface, becoming completely submerged, and then emerges at the head of a column of adherent liquid with the upper portion apparently unwetted by the liquid with which it has been covered. When the water drops from an oar on the recover, we often get what are known as rolling drops² which depend on the presence of adsorbed air films and which are also sensitive to the presence of electrified substances.

If the surface of a sheet of water is covered with oil or with a scum of oily soot or of plankton organisms, a mist or fog may deposit drops on the surface which will be extremely persistent. This phenomenon is not at all uncommon at Lake Mendota at Madison and has frequently been observed elsewhere.³

Since soap-bubbles are hollow drops, they should behave in some respects like liquid drops, though not necessarily like drops of a pure liquid. It is possible to press two soap bubbles together with considerable force without causing them to coalesce;⁴ but if they are electrified slightly, they coalesce readily without bursting.

It is interesting to note that water will apparently remove a film of adsorbed air much more readily from a polished surface of ivory or marble than it will from a water surface;⁵ but we do not know whether this is true for all solids. Sakulka⁶ obtained somewhat different results with lead shot, but this may have been because they were not polished.

If a vapor is adsorbed by a liquid, it will condense to a liquid film at a temperature above that of the normal dew-point. Can-

¹ WORTHINGTON: *Proc. Roy. Soc.*, **34**, 217 (1882).

² OSBORNE REYNOLDS: *Chem. News*, **44**, 211 (1881); KAISER: *Wied. Ann.*, **53**, 681 (1894).

³ JUDAY: *U. S. Monthly Weather Review*, **44**, 65 (1916); NAKAMURA: *Jour. Meteorological Soc., Japan*, **36** (1917).

⁴ BOYS: *Phil. Mag.* **25**, 409 (1888).

⁵ WORTHINGTON: *Proc. Roy. Soc.*, **34**, 217 (1882).

⁶ DRUDE'S *Ann.*, **25**, 892 (1908).

ADSORPTION OF LIQUID BY SOLID

tor¹ realized this with water and mercury and Clark² with olive oil which is not a well-defined and reproducible liquid.

ADSORPTION OF LIQUID BY SOLID

If a liquid is adsorbed at a solid surface, it forms a liquid film and we say that it wets the solid. If a liquid is not adsorbed by a solid, it does not wet the latter. There has been a good deal of question whether the liquid meets the wall at a definite angle, the contact angle, or whether the contact angle is zero. Lord Rayleigh³ states definitely that in his opinion the contact angle is zero,⁴ and this must be true if we consider that the liquid is adsorbed by the solid. The formation of a liquid film over the surface of a wetted solid accounts for the generally accepted fact that the rise of a liquid in a capillary tube is independent of the nature of the walls of the tube. This has always seemed a very improbable state of things and one that could only be justified by the fact that it was so. The whole thing becomes quite simple when we consider that the rising liquid does not come in contact with the walls of the capillary tube at all.⁵ We are really dealing with the rise of a liquid in a liquid tube and it makes no difference what material is used to support the walls of the liquid tube. That this is the real explanation may be seen from the fact that concordant results are not obtained when a liquid is allowed to rise in a dry tube. To get good results it is important to immerse the tube in the liquid and then to raise it. Bigelow and Hunter⁶ claim that the nature of the walls does have an effect on the capillary rise; but their experiments were not done in a capillary tube.

On the assumption that the contact angle is zero, a thin film of liquid must rise to the top of the tube, irrespective of the height and diameter of the tube. This has been recognized explicitly by Lord Rayleigh.⁷ When the liquid does not wet the solid,

¹ Wied. Ann., **56**, 492 (1895).

² Proc. Am. Acad., **41**, 361 (1906).

³ Scientific Papers, **3**, 393 (1902).

⁴ Cf. HARKINS and BROWN: Jour. Am. Chem. Soc., **41**, 522 (1919).

⁵ RAYLEIGH: Scientific Papers, **3**, 421 (1902).

⁶ Jour. Phys. Chem., **15**, 367 (1911).

⁷ Scientific Papers, **3**, 523 (1902).

mercury and glass for instance, the assumption of a zero-contact angle leads to at least one awkward conclusion. The upper part of the meniscus is certainly not in contact with the glass and therefore none of the mercury is in contact with the glass. If we have a glass tube, infinitely long, closed at the bottom, and filled with mercury, we must conclude, if we are going to be strictly logical, that the column of mercury does not touch the glass at any point and that it stands alone, surrounded on all sides by a film of air, mercury vapor, or something which is not glass. Personally, I feel no desire to be so logical as that. It seems to me probable that at some point the force of gravity squeezes out all the vapor layer and that the mercury does come in contact with the glass. This is the more certain because we know that the mercury sometimes tends to hang in a freshly-made barometer and this could not happen if the mercury were not in contact with the glass.

For a liquid to wet a solid in the presence of air, the liquid must be adsorbed more strongly than the air and must displace it. Hofmann¹ gives a number of details as to the slowness with which some liquids displace adsorbed air from certain solids. In some cases heating is necessary to get quick results. Lycopodium powder is distinctly difficult to wet. Gum arabic adsorbs air strongly and is not wetted readily by water. If ground with alcohol, the alcohol displaces the air and then the gum is wetted more easily by water. The floating of metallic powders or of pieces of metal on water is due to the slowness with which water wets them. The Cape Cod lighter consists of a porous stone set in a brass handle. When this is dipped into a can of kerosene, the kerosene is sucked rapidly into the pores displacing the air. The light is taken out, lighted, and placed under the logs of a wood fire. The adsorbed kerosene burns for about ten minutes, enabling one to do away with paper and even kindling wood. Another interesting application of the adsorption of a liquid by a solid is the case of solidified bromine.² It consists of siliceous earth saturated with bromine, which can be driven out by heat.

Of more technical importance is the adsorption of fused magne-

¹ Zeit. phys. Chem., **83**, 385 (1913).

² BRAND: Zeit. anal. Chem., **26**, 222; Jour. Chem. Soc., **52**, 688 (1887). Cf. THORP: Outlines of Industrial Chemistry, 251 (1916).

tite by chromite.¹ The simple form of magnetite arc consists of a lower, negative, magnetite terminal and an upper non-consuming terminal of copper, of such size that it does not get so hot as to oxidize or evaporate, but sufficiently hot to avoid condensation of magnetite vapor. When the arc is struck, a pool of melted magnetite forms on the surface of the magnetite terminal and the arc-conductor issues from a depression in this melted pool. The straight magnetite arc flickers badly; but this can be overcome by mixing the magnetite with some more refractory material, such as chromite. The chromite remains solid and holds the melted magnetite as a sponge does water. In this way, these arcs have been made steady and thereby suitable for industrial use.

We are quite familiar with the fact that glass must be cleaned before it can be wetted satisfactorily by water; but it is not so well known that platinum is only wetted by mercury under special conditions.² "Mercury, which holds even a very little sodium in solution, has the power of wetting platinum in a very remarkable manner. The appearance of the platinum is quite similar to that presented by amalgamable metals in contact with mercury. But the platinum is in no wise attacked. Further, the amalgam may be washed off by clean mercury, and the latter will also continue to adhere closely to the platinum. All the phenomena of capillarity are presented between the two. The surface of the mercury in a platinum cup so prepared is quite concave; and a basin of mercury may be emptied if a few strips of similarly prepared platinum foil be laid over its edge—just as a basin of water may be emptied by strips of paper or cloth, and under the same condition, namely that the external limb of such capillary siphon be longer than the internal one. The sodium removes the oxide film and permits the mercury to come in contact with the platinum."

It is found that iron, copper, bismuth, and antimony are also wetted by mercury if their surfaces are first touched with sodium amalgam.

A few years later a technical application of this observation was made. Kirchman³ reports that sodium amalgam can be

¹ STEINMETZ: *Radiation, Light, and Illumination*, 110 (1909).

² GUTHRIE: *Proc. Roy. Soc.*, **13**, 458 (1864).

³ *Jour. Chem. Soc.*, **26**, 418 (1873).

used advantageously in simplifying the method of dry-gilding iron. Surfaces of iron and similar metals, even though oxidized, are immediately amalgamated by simply rubbing with amalgam. Gold chloride in concentrated solution is then applied quickly on the amalgamated surface, and the mercury volatilized by the heat of lamp or fire. A very uniform gilding is thus obtained, permitting a high polish. Corresponding results are obtained with silver and platinum salts.

Wald¹ has pointed out that there must be a lowering of the vapor pressure of a liquid, when a liquid wets a solid. Consequently, if water really wets ice, or if water rises in a capillary tube made of ice, the vapor pressure of dry ice will differ from that of wetted ice at the same temperature. This point is not taken into account in books on the phase rule because effects due to capillarity, gravity, etc., are usually ruled out explicitly.

The adsorption of a liquid film may introduce quite an error in the determination of the specific gravity of bodies when they are weighed in a highly divided state. As long ago as 1848 Rose² pointed out that platinum in the state of foil has a specific gravity between 21 and 22 while a value above 26 was found for platinum precipitated from the chloride by sodium carbonate and sugar. Similar though less extreme differences were found with gold, silver, and barium sulphate. This can be accounted for if we assume that the powder is not weighed alone in water but in conjunction with a film of condensed water.³

It was Edward Lear who wrote about the Jumblies who went to sea in a sieve. He considered that a nonsense rhyme; but modern science is almost equal to the problem, for we can carry water in a sieve. If we take a fine-meshed metal sieve and oil the meshes, air can still pass readily through the holes; but water does not wet the wires and consequently surface tension prevents it from passing through the holes.⁴ Gasolene may be freed from water by filtering through a 200 mesh metal sieve. We can carry water in such a sieve⁵ if we do not fill it too full;

¹ Zeit. phys. Chem., **7**, 514 (1891).

² Pogg. Ann., **73**, 1 (1848); Jour. Chem. Soc., **1**, 182 (1849).

³ See however JOHNSTON and ADAMS: Jour. Am. Chem. Soc., **34**, 563 (1912).

⁴ CHWOLSON: Lehrbuch der Physik, **1** III, 613 (1907).

⁵ CAMPBELL: Jour. Ind. Eng. Chem., **6**, 762 (1919).

but an oiled sieve is not a perfect substitute for a pail. This principle has received an important technical application in the shower-proofing of textile fabrics.¹ The fibers are coated with some water-repellent hydrocarbon, wax, or salt, in which case the fabric will be porous to air but will shed water up to a certain point.

All campers are familiar with the unpleasant fact that a tent will leak in a rain if one touches the canvas with one's finger. The tent is shower-proof and not water-proof. When one pushes against the tent, it either contracts or expands the air spaces. If the air spaces contract, air is driven out and when the finger is taken away, water enters. If the air spaces expand, water runs in. Either way the air is displaced at that point and water enters. What happens can best be seen from an analogy. If one dips a fountain pen filler into ink and presses the bulb, air is driven out and ink enters when the pressure is relieved. If one pinches the bulb before dipping the glass end into the ink, no air bubbles out but ink goes in as soon as the pressure is taken off. It makes no difference therefore whether one touches a tent from the inside or the outside. In either case, water is drawn into the pores of the fabric and the tent leaks continuously once the air is displaced. Awnings on a boat usually leak where they rest on a wooden or iron support. This is because there is always enough wind or vibration to be equivalent to the touching of the tent with the finger. For the same reason, a tent is apt to leak around the pole.

The reverse case is to be seen in the ordinary water wings. They are made of a fine-meshed fabric which is first thoroughly wetted so that a film of water is formed in the pores. The strength of this water film is so great relatively that one can blow up the water wings without the air escaping and the water wings will support a grown person without difficulty.

Ehrenberg and Schultze² point out that many powders, when once thoroughly dried, are not easy to wet. After a period of drought, drops of rain will often roll along the dust without wetting it. Even in the case of a shower the dust may be only wetted to a depth of less than a quarter of an inch. This is

¹ C. O. WEBER: *Jour. Soc. Dyers and Colourists*, **17**, 146 (1901).

² *Zeit. Kolloidchemie*, **15**, 183 (1914).

shown by Ehrenberg and Schultze to be due to the adsorbed air on the surface of the solid. Any treatment which cuts down the amount of adsorbed air makes the dust, or soot, or other substance, more easily wetted.

It is not easy to wet carbon black with water; but if the oily material is driven out by a preliminary treatment with superheated steam, carbon black is dispersed by water very rapidly and the liquid bubbles like soda water owing to the escape of the adsorbed air. If a 50 cc vessel is filled with good cocoanut charcoal and if water is then added until the vessel is full up to the mark, 150–200 cc of air will be driven off.

A case analogous to that of the oiled sieve holding water has been described by Lord Rayleigh¹ who found that a piece of iron gauze pressed down upon the flat bottom of a glass vessel, holding a shallow layer of mercury, remained on the bottom of the vessel and did not rise through the mercury. It is quite clear from this that one could carry mercury in an iron sieve. With sodium in the mercury the amalgam would run through the gauze. Rayleigh's experiment of course would not succeed if tried with sodium amalgam instead of with mercury.

Since the adsorption of liquids by solids is selective, it follows that one liquid will be adsorbed more by a solid than will a second liquid and that consequently the first will displace the second from contact with the solid. No systematic study of this phenomenon seems to have been made; but we know that kerosene will displace water in contact with copper and that water will displace kerosene in contact with quartz,² while alcohol will displace oil in contact with metal³ and linseed oil⁴ will displace water in contact with white lead. According to this, one should use a rag dipped in alcohol with which to wipe off a lamp and it is for this reason that we cover metal surfaces with vaseline or with a heavy oil to prevent rusting. Parkerized or phosphatized iron is said to owe its non-rusting properties to an oil film. In the kitchen, people wet the moulds before putting in corn starch or gelatine, and they butter the pans before making fudge, or grease

¹ Scientific Papers, 4, 430 (1903).

² HOFMANN: Zeit. phys. Chem., 83, 385 (1913).

³ POCKELS: Wied. Ann., 67, 669 (1899).

⁴ CRUICKSHANK SMITH: The Manufacture of Paint, 92 (1915).

the griddles before making flapjacks. It is claimed that aluminum griddles do not need to be greased because the air in the oxide film keeps the cakes from sticking; but the same reasoning ought to apply to frying-pans when used for the same purpose and apparently does not. In making pottery, it is the practice to oil the dies when making dust-pressed ware.¹ Infusorial earth is excellent² for cleaning glass plates for photographic purposes. Even very greasy plates become clean very rapidly when rubbed with infusorial earth moistened with water. Some of the methods of removing grease spots from clothes depend on selective adsorption.³

There are almost no quantitative data on selective adsorption. Graham⁴ made a few rough measurements on the selective adsorption of liquids by palladium. A piece of foil was immersed in a liquid for an hour and afterwards dried by pressure for a few seconds between folds of blotting paper. One thousand parts of palladium foil were found to retain 1.18 of water, 5.5 of alcohol, 1.7 of ether, 0.54 of acetone, 4.5 of glycerine, 3.5 of benzene, 10.2 of castor oil, and 18.1 of oil of sweet almonds. Quite recently Mathers⁵ has shown that lead adsorbs certain essential oils from aqueous solution.

Since the adsorption is selective, a vapor or liquid will be adsorbed more readily by one surface than by another. A striking application of this is to be found in the old daguerreotype process. The latent image is formed on a plate of silver coated with silver iodide and it is developed by means of mercury vapor. The mercury condenses on the places which have been exposed to light. I have seen a patched cement cellar floor on which moisture condensed so markedly on the weathered portion that it seemed as though a pipe had broken under the floor.

If the adsorption is very marked we may get intense strains.⁶ Gelatine is adsorbed so strongly by glass that the gelatine film on drying will often tear off the surface of the glass. On the other

¹ SIMCOE and SMITH: *Trans. Am. Ceramic Soc.*, **14**, 558, 567 (1912).

² KOLLER: *The Utilization of Waste Products*, 310 (1915).

³ LAKE: *Jour. Phys. Chem.*, **20**, 761 (1916).

⁴ *Jour. Chem. Soc.*, **20**, 275 (1867).

⁵ *Trans. Am. Electrochem. Soc.*, **31**, 271 (1917).

⁶ GRAHAM: *Jour. Chem. Soc.*, **17**, 320 (1864).

hand, it does not adhere to plates of mica or calcite. With agar-agar we get a state of things which appears to vary with the concentrations. Certain agar-agar jellies will adhere readily to glass while others apparently do not. People have claimed that the substitution of agar-agar for gelatine in photographic plates would be impossible on a technical scale, because the agar-agar film would slip off if the plates were set vertically to dry; but it is probable that this difficulty would be overcome if that were the only drawback.

The whole theory of adhesives depends in part on the fact that the cementing material adheres strongly to the two surfaces and hardens there. It is therefore possible that one agglutinant may be useful for a number of different materials, such as wood, glass, metal, ivory, etc., while others give good results only with special materials. Since the books give different recipes for cements for glass, cements for metals, cements for metals and glass, etc., the differences in adsorption are real ones though no one has ever made a careful study of agglutinants from this point of view.

A good glue joint in wood will easily stand a strain of 6000 lbs. per square inch. We are quite familiar with this; but we do not always realize that the tensile strength of liquid water is pretty high if a decrease in the cross-section can be prevented. As far back as 1850 Berthelot¹ filled a glass tube nearly full of liquid, removed the air, sealed the tube, heated the tube until it was entirely full of liquid, and allowed the whole thing to cool. The liquid continued to fill the tube until the volume was larger than it should be for the temperature by $1/420$ in the case of water, $1/93$ in the case of alcohol, and $1/50$ in the case of ether. This indicates a breaking strain of about 50 atm. for water and over 100 atm. for alcohol and ether. Worthington² obtained 17 atm. for alcohol. Stefan³ and Tumlrir⁴ consider that the calculated internal pressure of a liquid is a measure of the theoretical tensile strength and they obtain in this way a value for alcohol⁵ of about 2000 atm. Some direct measurements of the tensile

¹ Ann. Chim. Phys. (3) **30**, 232 (1850).

² Phil. Trans., **183A**, 355 (1892).

³ Wied. Ann., **29**, 655 (1896).

⁴ Sitzungber. Akad. Wiss. Wien, **109** IIa, 837 (1900); **110** IIa, 437 (1901).

⁵ Cf. HULETT: Zeit. phys. Chem., **42**, 353 (1903).

strength of liquid films have recently been made by Budgett,¹ who found a maximum breaking strength of about 87 pounds per square inch for steel end-gauges held together by a water film. On the assumption that the water occupied only one-tenth of the surface, this gives a tensile strength of nearly 900 pounds per square inch, or about sixty atmospheres.

Rice² reports that certain plastic clays from Montana, when worked in the brick-making machines adhered to iron in a remarkable way whenever they came into contact with that metal. Rice does not explain why these clays should stick to iron. One of the clays was very high in silica, 76.8 percent.

The formation of glazes on pottery and still more of enamels on metals are cases in which the fused or sintered mass must not only adhere to the base after cooling but must also have nearly enough the same coefficient of expansion to prevent the glass or enamel from going to pieces as the temperature changes.³

The adsorption of water vapor by gelatine presents some peculiarities. Working in Ostwald's laboratory, von Schroeder⁴ found that gelatine contained a thousand percent of water when immersed in liquid water and less than 400 percent when in saturated water vapor at the same temperature. From these and other experiments von Schroeder concluded that the vapor pressure of water in gelatine must be higher than that of pure water, because water distills from the gelatine to the vapor phase. The reason for this unexpected phenomenon is possibly that gelatine has a cellular structure. If a dry paper bag be placed in a space saturated with water vapor, the paper will adsorb a certain amount of water; but there will be little or no tendency for the water to condense inside the bag and fill it with liquid water. If a similar bag is immersed in liquid water, the paper will take up water as before; but water will also pass into the bag and fill it. If the bag is then lifted into the vapor phase, and if the bag is so constructed that the actual dripping is negligible, the water will distill from the curved surface in the bag to the

¹ Proc. Roy. Soc., **82A**, 25 (1912).

² Trans. Am. Ceramic Soc., **14**, 610 (1912).

³ RANDAU: Enamels and Enamelling, 101 (1912).

⁴ Zeit. phys. Chem., **45**, 109 (1903).

plane surface in the containing vessel. The smaller the bag is, the greater will be the curvature of the water within and consequently the higher the vapor pressure. With the microscopic spaces in solidified gelatine, the vapor pressure of the drops of water will be enough higher to counterbalance the difference of levels in von Schroeder's experiments.

While this explanation accounts for the phenomena provided gelatine really has a cellular structure, a point which is not yet generally accepted—it is superfluous if the facts are not as stated. Wolff and Buchner¹ claim that the loss of water when gelatine is placed in the vapor phase is merely due to experimental error.² They have certainly shown the possibility of error in von Schroeder's results; but they did no experiments involving as much error as one must assume if von Schroeder's data are worthless. The whole matter is therefore up in the air for the present. Washburn³ found that moistened clay will dry pretty completely if suspended in a closed vessel above water. He attributes this to the action of gravity. This could only be true in case there were no soluble salts in the clay and in case the pores were so coarse that the capillary rise was not equal to the distance above the water level.

There are other substances which seem to behave like gelatine, though no experiments like von Schroeder's have been performed. Schwalbe⁴ states that cotton cellulose takes up 21 percent moisture in presence of saturated water vapor. Masson and Richards⁵ find 17.7 percent adsorbed moisture when the vapor phase is 97 percent saturated. By extrapolation to 100 percent this might easily give about 21 percent moisture; but Masson and Richards incline to the view that the curve is asymptotic, in which case the value would be infinite, which seems absurd. Vignon⁶ finds that one gram of cotton takes up about five grams of liquid water, while a fine-grained sponge will hold thirty grams of water per gram of sponge, and a coarse-grained sponge

¹ Kon. Akad. Wet. Amsterdam, **17**, May 30 (1914); Zeit. phys. Chem., **89**, 271 (1915),

² See also ARISZ: Kolloidchemische Beihefte, **7**, 87 (1915).

³ Jour. Am. Ceramic Soc., **1**, 25 (1918).

⁴ Die Chemie der Cellulose, 10 (1911).

⁵ Proc. Roy. Soc., **79A**, 421 (1906).

⁶ Comptes rendus, **127**, 73 (1898).

only about six grams. Leighton¹ states that absorbent cotton will hold four grams of water when centrifuged at 4000 R.P.M. Some of this water is held in capillary spaces; some is adsorbed on the surface of the cotton; a part is probably dissolved in the cotton; and some may be held in cells. We have no satisfactory way of differentiating between these possibilities.

Dry caseine takes up about 1.25 g water per gram of caseine.² Infusorial³ earth is able to take up more than double its weight of liquid. Wood flour will take up over double its weight of nitroglycerine without running.⁴ Fibrous peat, fresh from the bog, may contain 90 percent of water and Sphagnum moss may imbibe as much as two hundred times its own weight of water,⁵ which is the reason that this moss is used largely in the trenches for dressing wounds.

If a freshly-broken piece of porous earthenware be pressed against the tongue, water will be sucked up into the pores of the earthenware and the piece will tend to stick to the tongue. When water is drawn up into a capillary space, air is driven out and one at once wonders how much pressure the water will exert under these circumstances. Jamin⁶ has made some preliminary experiments along this line. A hole was bored in a piece of dried chalk. Into this hole was dipped one end of a manometer and the hole was then closed. When the chalk was placed in water, the air was displaced from the pores and a pressure of 3-4 atmospheres was obtained. This is not the limiting pressure because the amount of dead space in the manometer was large. A better method would be to determine the pressure necessary for the air to force the water out of the pores of the chalk.

Spring⁷ obtained pressures of one-fifth of an atmosphere when water displaced air in contact with sand.

Jamin, Askenasy, and Wiedeburg⁸ have described different

¹ Jour. Phys. Chem., **20**, 32 (1916).

² VAN SLYKE and PUBLOW: Science and Practice of Cheese-Making, 179 (1913).

³ KOLLER: Utilization of Waste Products, 310 (1915).

⁴ KRESSMAN: Met. Chem. Eng., **14**, 372 (1916).

⁵ Percy's Metallurgy: Fuel, 208 (1875).

⁶ CHWOLSON: Traité de Physique, 1 III, 622 (1907).

⁷ Mem. Soc. belge Geologie, **97**, 13 (1903).

⁸ Wied. Ann., **59**, 764 (1896).

forms of apparatus in which water evaporates through a porous tube or a porous cup of plaster into dry air. As the water evaporates off, mercury is drawn up into the tube reaching a height of 90 cm without difficulty. If bubbles of air did not form, water or mercury could be drawn up to incredible heights, limited by the tensile strength of the liquids.

When considering the adsorption of water vapor by cotton, reference was made to the heat developed. Attention might perhaps be called here to Meissner's experiments on the heat developed when powders are wetted by liquids.¹ He found that there was no appreciable difference in the heat evolved when water was taken above and below 4°. His quantitative results were rather discouraging, however, because he found no apparent relation between the amounts of heat evolved and the amounts of powder taken, which must be the result of experimental error. The more careful experiments of Parks² showed that when silica, sand or glass is brought in contact with water at approximately constant temperature, the development of heat at 7° is approximately 0.00105 cal. per square centimeter of surface wetted.

Foote and Saxton³ find that water adsorbed by lamp-black supercools readily to -6° and is not all frozen at -35°. When once frozen, the water does not begin to melt until nearly 0° in the case of lamp-black. Water adsorbed in gelatinous precipitates may start melting at -20°. McIntosh and Edson⁴ find that when a salt solution is plunged into liquid air or solid carbon dioxide, the resulting solid forms a constant-melting mixture, melting completely at the temperature at which the solution should have started freezing. It is not clear why this should be so.

ADSORPTION OF SOLID BY SOLID

Dried glue may be considered either as a solid or as a supercooled liquid. If we consider it as a solid, then the adsorption of gelatine by glass is a case of adsorption of a solid by a solid. It is more satisfactory to have cases where there can be no doubt

¹ MEISSNER: *Wied. Ann.*, **29**, 114 (1886).

² *Phil. Mag.* (6) **4**, 247 (1902).

³ *Jour. Am. Chem. Soc.*, **33**, 588 (1916); **39**, 627 (1917).

⁴ *Ibid.*, **38**, 613 (1916).

but that both substances are solids. We get marked adsorption of rouge by metals.¹ If a metal is polished with rouge which is not kept sufficiently moist, the rouge adheres so firmly to the metal surfaces that it cannot be removed without spoiling the polish. Blue powder is another case of adsorption. Here we have grains of zinc coated with zinc oxide which adheres even when the zinc is melted. Aluminum and nickel are always coated with solid surface films which have marked effects on the properties of the metals. Passive iron owes its peculiar properties to the adsorption and stabilization of a higher oxide,² either FeO_2 or FeO_3 . It seems probable that vermilion is adsorbed by copper because De la Rue³ says that electroplated copper blocks cause vermilion to blacken while cast copper does not.

We get what seems to be a case of adsorption of a solid by a solid if we shake a moderately coarse powder with a much finer powder. Instead of the finer powder filling the voids in the space occupied by the coarse powder, the former tends to coat the latter.⁴ If the two powders are of different colors, the color of the coarser powder may be masked completely by a relatively small amount of the fine powder. In one experiment 0.032 g of Prussian blue was mixed with 10 g dolomite which passed a 40 mesh sieve and did not pass a 100 mesh sieve. In the second experiment the same amount of Prussian blue was mixed with 10 g dolomite, all of which would pass a 200 mesh sieve. In the first case, the powder was a deep blue and in the second it was practically white, though the percentage compositions were the same in the two cases. In another experiment 1 percent Fe_2O_3 colored the dolomite a full red when the rouge passed a 200 mesh sieve and the dolomite did not pass a 100 mesh sieve. When the dolomite passed a 200 mesh sieve and the iron oxide did not pass a 100 mesh sieve, the powder was practically white. In a third set of experiments 8 milligrams of lamp-black blackened 10 g dolomite which was coarser than 40 mesh. When the dolomite was ground so that it all passed a 200 mesh sieve, 654

¹ DESCH: *Metallographie*, 210 (1914).

² BENNETT and BURNHAM: *Jour. Phys. Chem.*, **21**, 107 (1917).

³ *Mem. Chem. Soc.*, **2**, 305 (1845).

⁴ FINK: *Jour. Phys. Chem.*, **21**, 32 (1917); BRIGGS: *Ibid.*, **22**, 216 (1918).

milligrams of lamp-black, or over eighty times as much, were needed to produce approximately the same tint.

This behavior of powders is of great importance when using inert fillers in mixed paints.¹ The amount of barytes that can be mixed with colored pigments without injuring them is remarkably large. There are hundreds of brands of para-red paints made and consumed every year by the agricultural implement trade which contain as high as 90 percent of natural barytes. The opacity of paper may be increased by grinding the filler more finely.

Fink has shown that a given mixture of a white non-conducting powder like thoria with a black conducting powder like tungsten may either be black and conduct electricity or white and a non-conductor, depending on the relative coarseness of the two powders. If one strews lycopodium powder over the surface of water and then puts one's finger into the water, the lycopodium powder sticks to the finger and keeps it from being wetted.² A coarse powder kept in a bottle will fall to the bottom of the bottle through the force of gravity while a very fine powder will stick to the walls of the bottle discoloring them. Writing on paper with a pencil or on a blackboard with chalk is a phenomenon of about the same type, though the matter is simplified by the roughened surface on which one writes. Solid particles are rubbed off and stick. It seems probable that the possibility of using face powder is merely a special case of a very fine powder adhering to a curved surface.

In phosphate baking powders, the monocalcium phosphate is protected from moisture by an admixture of starch and it is well-known in the trade that the calcium phosphate must not be too fine nor the starch too coarse; potato starch cannot be substituted for corn starch. The retarding effect on the rate of setting of Portland cement, which is produced by the addition of gypsum is probably due to the fact that the finer gypsum powder coats the coarser cement powder and acts to some extent as a protecting film.

In all these cases the powders do not come in actual contact, but are separated by a film of air which, however, holds them

¹ TOCH: *The Chemistry and Technology of Paints*, 113, 138 (1916).

² EHRENBERG and SCHULTZE: *Zeit. Kolloidchemie*, 15, 183 (1914).

ADSORPTION OF LIQUID BY SOLID

together, thus behaving like a liquid film. Traces of moisture increase the adhesion, as in the case of sugar and blueberries. The fine particles will be held more firmly in hollows in the coarser powders than on projections and will therefore accumulate first in the concave portions, next on the plane surfaces, and last of all on the convex surfaces. Aitken¹ found that hot powders adhered to a cold rod of glass or metal; but fell off when powder and rod were of the same temperature and were repelled when the rod was hotter than the powder. This is due to a lowering of the surface tension of the condensed air film on the hotter side of the powder. It is necessary to work with such coarse particles that they fall off under the influence of gravity except when special conditions prevail.

It has been shown that the time factor is an important one in the wetting of some solids by some liquids, the air film being displaced slowly. It is possible that in some cases adhering powders displace the air film slowly and become really adsorbed by the supporting solid.

ADSORPTION OF LIQUID BY LIQUID

The spreading of one liquid over another is usually considered to depend on the relative surface tensions. If oil is dropped on water, it is assumed that we have a water-air surface, a water-oil surface, and an oil-air surface as shown in Fig. 4. If the surface tension water-air is greater than the sum of the surface tensions oil-water and oil-air, the drop of oil spreads out over the surface of the water. If the water-air surface tension is less than the sum of the other two the oil will draw up into a globule. While this may be a perfectly correct way of looking at things, it is not a useful one because Rayleigh² claims that three fluids cannot be in contact simultaneously. The simplest way to look at the

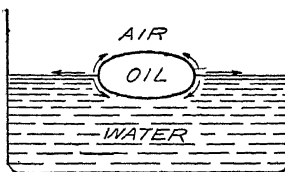


FIG. 4.

¹ Trans. Roy. Soc. Edin., **32**, 239 (1884); TAMMANN: *Drude's Ann.*, **18**, 856 (1905).

² Scientific Papers, **3**, 354, 413, 416 (1902).

matter is to consider the adsorption. If oil is adsorbed by water, it wets the water and spreads over the surface. Now the adsorbed layer may be very thin, not over $2\mu\mu$ in some cases. At greater thicknesses there is nothing to prevent the oil tearing loose from the oiled surface of the water and drawing up into drops under the influence of surface tension. This has been commented on by Rayleigh¹ and by Budgett.²

The first portion of oil spreads over the water because it is adsorbed and held by the water. The second portion of oil flows out over the oiled surface, but is instable because the same mass of oil would have a less surface if present in drops and still more so if present in a single drop. The excess oil therefore draws up into one or more drops depending on conditions, thereby leaving bare oiled surfaces. The several drops will coalesce into one large one if brought in contact. If more oil is added the drops become larger and finally form so large a drop that under the influence of gravity, it covers the whole surface of the water and becomes a liquid layer of free oil. From this way of looking at it, we see that the phenomenon must be general and so it is. Budgett³ found that it was quite impossible to get a thin continuous film of kerosene or water on the surface of steel blocks. Microscopic examination showed that the applied films were not continuous membranes but that the liquid collected into small drops. This is undoubtedly exactly like Rayleigh's experiment. On the surface of the wetted steel the kerosene or water gathered in small drops. With different liquids, we should expect to find the drops first forming when the films reached different thicknesses. This has been noted by Hardy⁴ who found that the thickness of the oil film varied from $2-200\mu\mu$ with different oils. With one sample of oil there was apparently no spreading at all.

If an oil is not adsorbed by water, there is theoretically a film of air between the water and the drop of oil. It seems improbable that this air film can continue to exist when a thick layer of oil is present and yet, if not, there must be some point under some

¹ Scientific Papers, **3**, 424 (1902).

² Proc. Roy. Soc., **85A**, 30 (1911).

³ Ibid., **86A**, 30 (1911).

⁴ Ibid., **86A**, 612 (1912).

ADSORPTION OF LIQUID BY SOLID

conditions when surfaces of oil, water, and air coexist. It seems probable that Rayleigh's conclusion, that such a state of things cannot exist, holds only when the effect of gravity is ignored. With increasing amount of oil there probably comes a time when the air film is squeezed out entirely. The breaking up of a liquid film into drops has been paralleled by the behavior of thin solid films when heated. Beilby¹ showed that a very thin film of gold leaf became granular if heated moderately.

ADSORPTION OF SOLID BY LIQUID

A solid which is wetted by a liquid, adheres to that liquid. With two liquids and one solid we get selective adsorption of the solid and this leads to some interesting results, which have been studied carefully by Hofmann.² If finely divided red lead is shaken with water and benzene or chloroform, the red lead adheres to the surface of the benzene or chloroform, making a practically continuous coating around the organic liquid provided proper relative amounts of red lead and organic liquid are taken. The theory of the phenomenon has been given by Des Coudres.³ The solid particles tend to go into the water phase if they adsorb water to the practical exclusion of the other liquid; they tend to go into the other liquid phase if they tend to adsorb the other liquid to the practical exclusion of the water; while the particles tend to go into the dineric interface in case the adsorption of the two liquids is sufficiently intense to increase the miscibility of the two liquids very considerably at the surface between solid and liquid.

Of course the powder will only stay in the upper phase or the dineric interface in case it is so fine that the adsorption overbalances gravity. These conclusions as to the way a given pair of liquids will behave with a given solid refer to the relations prevailing under the conditions of the experiment. Hofmann's experiments with two liquid layers in glass test-tubes (soda-lime glass) showed that the time factor might be an important one. If a few cubic centimeters of an aqueous potassium bichromate

¹ Proc. Roy. Soc., **72**, 226 (1904).

² Zeit. phys. Chem., **83**, 385 (1913).

³ Arch. Entwicklungsmechanik, **7**, 325 (1898).

solution are shaken up in a carefully cleaned glass test-tube, there remains on the walls of the test-tube a continuous uniform coating of solution recognizable by its yellow color. This film gradually becomes thinner and paler but does not break at any point until the water disappears completely through evaporation. If one adds a layer of xylene or kerosene to the aqueous bichromate solution in the test-tube, it is easy to see that there is a coating of aqueous solution between the organic liquid and the glass. If water is allowed to flow in at the bottom of the test-tube, the organic liquid can be forced out at the top and there will be no sign of its having adhered to the glass wall at any point. If, however, the test-tube containing the aqueous bichromate solution and the xylene or kerosene be left standing quietly for a long time, 6-10 hours, it will be found that the organic liquid has diffused through the water film to some extent and now adheres to the glass wall nearly everywhere, having displaced the aqueous film almost completely. If the contents of the test-tube are shaken violently, the water displaces the organic liquid from the glass surface practically completely. The glass is therefore wetted more readily and more rapidly by water than by xylene or petroleum; but a large mass of xylene or petroleum will gradually displace a water film from the glass surface. One would therefore expect to get a slightly different behavior with glass powder according as one treated it first with water or with organic liquid. This was exactly what Hofmann found. If the glass powder were treated first with water and then shaken with kerosene, practically all the glass went into the water phase. If the glass powder were allowed to stand a long time with kerosene, or if it were heated with it to hasten the removal of the air film, some of the glass powder would remain in the dineric interface. Vigorous shaking would, of course, cause the water to displace the kerosene. Chloroform behaves towards glass and water somewhat like xylene or kerosene though the tendency to displace the water layer from the glass is less than with kerosene. Small drops of chloroform do not break through the water film at all. With increasing amounts of chloroform the force of gravity causes it to break through at the bottom of the test-tube, the surface wetted by the chloroform increasing as the column of chloroform increases in height.

ADSORPTION OF LIQUID BY SOLID

In Table XIX are given some of Hofmann's results. The letter *w* means that the solid goes nearly completely into the water phase; while *o* denotes that it goes almost completely into the organic liquid; *s* means that the powder collects nearly quantitatively in the interface. Two letters, such as *sw*, mean that the powder goes partly into the interface and somewhat less into the water phase; the use of a parenthesis, *s(w)* or *s(o)*, signifies that there is a good deal more powder in the interface than in the bracketed phase. Benzene and xylene behave alike so only one is given. In the experiments tabulated, the powder was placed in water and then shaken with the organic liquid.

TABLE XIX.—PREFERENTIAL WETTING OF SOLIDS

Water and	Ether	Chloro- form	Butyl alco- hol	Benzene	Kero- sene	Amyl alco- hol	Paraffin oil
CaSO ₄	<i>w</i>	<i>w</i>	<i>w</i>	<i>w</i>	<i>w</i>	<i>w</i>	<i>w</i>
SnO ₂	<i>w(s)</i>	<i>ws</i>	<i>ws</i>	<i>s(w)</i>	<i>s(w)</i>	<i>sw-</i>	<i>sw</i>
Al(OH) ₃	<i>w(s)</i>	<i>ws</i>	<i>ws</i>	<i>s</i>	<i>s(w?)</i>	<i>sw</i>	<i>s(w)</i>
SnS	<i>ws</i>	<i>ws</i>	<i>ws</i>	<i>s(w)</i>	<i>s(w)</i>	<i>s</i>	<i>ws</i>
BaSO ₄	<i>ws</i>	<i>ws</i>	<i>ws</i>	<i>s</i>	<i>s</i>	<i>s(w?)</i>	<i>s(w?)</i>
ZnS	<i>w(s)</i>	<i>ws</i>	<i>ws</i>	<i>s</i>	<i>s(w?)</i>	<i>s</i>	<i>s(w?)</i>
ZnO	<i>ws</i>	<i>ws</i>	<i>s(w)</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
CaCO ₃	<i>ws</i>	<i>ws</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
Mg(OH) ₂	<i>s(w?)</i>	<i>ws</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s(w)</i>	<i>sw</i>
Al	<i>sw</i>	<i>s(w)</i>	<i>s(w)</i>	<i>s</i>	<i>s</i>	<i>s(w)</i>	<i>s</i>
BaCO ₃	<i>ws</i>	<i>ws</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>sw</i>	<i>s</i>
CuS	<i>ws</i>	<i>s(w)</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
PbCrO ₄	<i>ws</i>	<i>s(w?)</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
Cu ₂ O(?)	<i>ws</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
MoS ₂	<i>s(w?)</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
PbS	<i>ws</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
Fe ₃ O ₄	<i>ws</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
BaCrO ₄	<i>ws</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
Pb ₃ O ₄	<i>sw</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
C	<i>sw</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
PbI ₂	<i>s</i>	<i>s</i>	<i>os</i>	<i>s</i>	<i>s</i>	<i>os</i>	<i>s</i>
HgS	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
HgO	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
HgI ₂	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>o</i>	<i>os</i>
AgI	<i>s</i>	<i>s</i>	<i>o</i>	<i>s</i>	<i>s</i>	<i>o</i>	<i>os</i>

Much the same conclusions have been worked out by Reinders¹ independently of Hofmann. Some of his data are given in Table XX. The powder was placed in the water phase and then shaken with the organic liquid.

TABLE XX.—PREFERENTIAL WETTING OF SOLIDS

Water and	Paraffin oil	Amyl alcohol	CCl ₄	Benzene	Ether
Kaolin	<i>w</i>	<i>w(s)</i>	<i>w(s)</i>	<i>w</i>	<i>w(s)</i>
CaF ₂	<i>ws</i>	<i>ws</i>	<i>w(s)</i>	<i>w(s)</i>	<i>w(s)</i>
Gypsum	<i>w</i>	<i>ws</i>	<i>w</i>	<i>sw</i>	<i>ws</i>
BaSO ₄	<i>w(s)</i>	<i>ws</i>	<i>ws</i>	<i>sw-</i>	<i>ws</i>
Magnesium	<i>ws</i>	<i>ws</i>	<i>ws.</i>	<i>ws</i>	<i>ws</i>
PbO	<i>s</i>	<i>s</i>	<i>sw</i>	<i>s</i>	<i>sw</i>
Malachite	<i>so</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>sw</i>
ZnS	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>sw</i>
PbS	<i>so</i>	<i>so</i>	<i>s</i>	<i>s</i>	<i>s</i>
HgI ₂	<i>so</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
Carbon	<i>so</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
Selenium	<i>so</i>	<i>so</i>	<i>so</i>	<i>s</i>	<i>s</i>
Sulphur	<i>so</i>	<i>so</i>	<i>o(s)</i>	<i>so</i>	<i>s</i>

Similar results were obtained with colloidal solutions, Isobutyl alcohol was added to a colloidal gold solution obtained by reducing gold chloride with carbon monoxide. When the two liquids are shaken, the gold forms a thin film at the interface. This film is violet blue to blue green by transmitted light and golden by reflected light. A thin water film forms between the isobutyl alcohol and the glass, and the gold concentrates in the dineric interface thus formed, making the alcohol appear uniformly gold-plated. With ether the gold film rises high above the level of the two liquids. With carbon bisulphide the adherent film of gold appears blue. When the carbon bisulphide is broken into drops by shaking, each drop appears blue. When a blue gold was obtained by reducing gold chloride with phosphorus dissolved in ether, the gold went into the dineric interface. When a brownish red gold was obtained in this way, it remained in the water phase and showed no tendency to pass into the interface. This difference is undoubtedly due to an adsorption of something at the

¹ Zeit. Kolloidchemie, **13**, 235 (1913).

surface of the gold because Reinders found that 0.005 percent gum arabic prevents colloidal gold from passing into the ether-water interface. With carbon tetrachloride, carbon bisulphide, and benzene, the gold goes to the interface as before; but the gum arabic prevents its changing from red to blue.

With colloidal ferric oxide practically no iron went into the interface with any of the organic liquids. It seems probable that this is due to Reinders using a ferric oxide solution which was a year and a half old, because hydrous ferric oxide is ordinarily a pretty good emulsifying agent.¹ Colloidal arsenic sulphide goes into the dineric interface with amyl alcohol or butyl alcohol; but stays in the water phase when carbon tetrachloride, benzene, or ether is the second liquid. India ink goes completely into the interface with isobutyl alcohol and stays entirely in the water phase when ether is the second liquid. When crystallized copper eosinate is placed in water and shaken with ether, it goes entirely into the surface between the two layers,² giving a film which resembles the purple skin of a grape, by reason of the steel-blue color of the crystals.

An interesting experiment is to shake copper powder or aluminum powder with kerosene and water. The metallic powder goes into the kerosene and into the interface, producing an effect of molten copper or molten aluminum as the case may be. When the bottle is allowed to stand after having been shaken, the metallic powder in the interface creeps up the side of the bottle above the surface of the liquid, rising higher if a little alcohol has been added. I have seen an apparently coherent metallic film rise two or three inches above the surface of the upper liquid phase. If too much copper or aluminum be added the kerosene cannot hold it all up and a portion falls to the bottom of the flask carrying drops of kerosene with it. If the mixture be poured out on a piece of wood, the copper spreads over the surface of the wood just as it did over the surface of the glass. This experiment illustrates the principle involved in all bronzing liquids. A bronzing liquid consists of a volatile liquid which will hold up the metal, and some substance which will keep the metallic powder from rubbing off too readily after it has been applied.

¹ BRIGGS: Jour. Phys. Chem., **19**, 296 (1915).

² GILBERT: Jour. Phys. Chem., **18**, 602 (1914).

The second substance also serves the purpose of keeping the metallic powder in a better state of suspension in the volatile liquid. According to Worden¹ the best of these bronzing liquids consist essentially of pyroxylin dissolved in amyl acetate, to which the metallic powder is added. For bronzing radiators and steam pipes, a pure pyroxylin would not do since it would decompose, disintegrate, and allow the metallic coating to peel off. To prevent this, boiled linseed oil and rosin may be added. Such preparations are of course much slower in drying than pyroxylin bronzing liquids; but that is not a serious objection for these special purposes. A much cheaper form of bronzing liquid consists of rosin dissolved in benzene, while the cheapest of all is apparently a solution of sodium silicate in water. The aluminum and copper powders on the market are coated with stearin; but special experiments in my laboratory have shown that the behavior of copper and aluminum with kerosene is the same qualitatively whether the stearin coating is removed with ether or not.

Barus² and Rayleigh³ have each noticed that when fine powders (bole) or dust are shaken with ether and water the solid particles go into the water layer, leaving the ether layer astonishingly clear. In fact Rayleigh said that the ether layer was more free of motes than he had ever been able to obtain by repeated distillation of liquid in vacuum. White lead passes from water into linseed oil.⁴ "During recent years the practice has been adopted largely among white lead corrodors who grind their own white lead in oil of doing away with the final drying of the white lead pulp as it comes from the washing process, and grinding or beating up the pulp (exhausted of water until the proportion of the latter does not exceed about 20 percent) with a suitable quantity of refined linseed oil. This process depends on the greater surface attraction which white lead particles offer to linseed oil than to water. It enables considerable economies to be effected in the manufacture of 'ground white lead' and it eliminates risk of lead poisoning during one of the most dangerous

¹ Nitrocellulose Industry, **1**, 310-320 (1911).

² Am. Jour. Sci. (3) **37**, 124 (1889).

³ Scientific Papers, **3**, 569 (1902).

⁴ J. CRUICKSHANK SMITH: The Manufacture of Paint, 92 (1915).

parts of the white lead manufacturing process." Zinc oxide stays in the water phase. The Elmore bulk-oil process of ore flotation depended on the fact that some sulphide ores can be shaken out of the water phase by means of suitable oils while the gangue stays in the water phase. When ground bituminous coal is stirred up with fuel oil and water, there is a good separation of coal from ash, the former going into the oil and the latter into the water. The readiness with which solid films form over the surface of mercury is well known to everybody. Salts of mercury or of the baser metals coat mercury with great readiness, especially in the air.

CHAPTER III

ADSORPTION FROM SOLUTION

ADSORPTION FROM SOLUTION BY SOLID

Selective adsorption by a solid from a solution may show itself by relatively more of the dissolved substance being adsorbed than of the solvent, or by relatively less being adsorbed. In the first case, commonly called positive adsorption, the solution becomes more dilute and in the second case, commonly called negative adsorption, the solution becomes more concentrated. Both cases are known; but the first one is the more important and will be considered now. The decolorizing action of charcoal¹ has been known since 1791. In 1874 Böttger² pointed out that when an alcoholic solution of any of the aniline dyes is shaken up with a sufficient quantity of infusorial earth, some water added, and the whole thrown on a paper filter, the liquid which runs through is perfectly colorless, the pigment being retained by the siliceous earth. The adsorption of dyes by hydrous alumina, stannic oxide, and other mordants as they are called, is of great importance in dyeing. Here as in all other cases the adsorption is selective. Davison³ showed that when alumina is precipitated from an aluminum acetate solution, it will decolorize dilute solutions of alizarine, alizarine green, benzo orange, and acid violet: it adsorbs fast green, acid green, and croceine orange considerably, and has practically no adsorbing action on emerald green or chrysoidine. Red phosphorus will decolorize a dilute solution of iodine in carbon bisulphide.⁴

Hatschek⁵ points out that iodides cannot be shown to be present in sea-water by any of the usual tests, and that we owe our supply of iodine to the adsorption of iodides by certain sea-weeds.

¹ Cf. OSTWALD: *Lehrbuch allgem. Chemie*, 2nd. Ed., 1, 1093 (1891).

² *Jour. Chem. Soc.*, 28 170 (1875).

³ *Jour. Phys. Chem.*, 17, 737 (1913).

⁴ SESTINI: *Gazz. chim. ital.*, 1, 323; *Jour. Chem. Soc.*, 24, 1006 (1871).

⁵ *An Introduction to the Physics and Chemistry of Colloids*, 6 (1913).

When making density determinations¹ by weighing a solid in a solution, an error may be introduced because of the solid adsorbing some of the salt. This error is likely to be larger the finer the particles of the solid, because the ratio of surface to mass increases with increasing subdivision. With grains of quartz or glass varying in diameter from 0.015 mm to 0.9 mm, placed in solutions of iodides, the specific gravity of the latter can be adjusted so that the smaller particles will sink while the larger will float. Marble is so porous that its surface is almost proportional to its volume, and consequently grains of marble do not show this phenomenon.

According to Skey² antimony and arsenic can be removed so completely from solutions of their oxides or chlorides in moderately strong hydrochloric acid (with a little tartaric acid in the case of antimony) by charcoal that neither of them can be detected therein by Reinsch's test, although before the treatment they could be detected without difficulty. Commercial sulphuric and hydrochloric acids diluted with a little water can be purified from either of these substances by agitating them intermittently for a short time with fresh charcoal, and then filtering off; application of heat to the mixture expedites this result.

Quite recently Lockemann and Paucke³ have studied quantitatively the adsorption of arsenic acid by charcoal, hydrous aluminum oxide, hydrous ferric oxide, and albumin. They find that egg albumin and blood serum, when coagulating, carry down certain amounts of arsenic from aqueous solutions. Animal charcoal also adsorbs some amounts of arsenic from aqueous solutions. When hydrous aluminum oxide is precipitated by ammonia, it carries down very appreciable quantities of arsenic. Curiously enough more arsenic is carried down when the hydrous aluminum oxide is precipitated from hot solution than when precipitated from a cold one. This unexpected fact is probably due to the form in which the alumina is precipitated. At the temperature of the water-bath, arsenic in amounts up to 20 mg As per 100 cc can be precipitated completely but this requires the use of very

¹ THOULET. *Comptes rendus*, **99**, 1072 (1884); *Jour. Chem. Soc.*, **48**, 476 (1885).

² *Chem. News*, **17**, 157 (1868); **36**, 6 (1877).

³ *Zeit. Kolloidchemie*, **8**, 273 (1911).

large amounts of alumina. When precipitated by ammonia, hydrous iron oxide carries down large amounts of arsenic, more being carried down the lower the temperature and the smaller the excess of ammonia. When the concentration of arsenic does not exceed 10 mg As per 100 cc it can easily be precipitated quantitatively by means of iron.

In 1845 Yorke¹ discussed the adsorption of lead oxide by filter paper, while Müller² and Weiske³ have shown that filter paper takes up such appreciable quantities of barium, strontium and calcium hydroxides that dilute solutions of these salts should not be filtered if they are to be used for quantitative work.

A special phenomenon in connection with adsorption by filter-paper has been studied by Bayley,⁴ Lloyd,⁵ Gordon,⁶ and others.⁷ If a drop of a salt solution be allowed to fall on filter-paper the solution will tend to spread. If the salt is adsorbed very strongly it will not spread and we get a relatively wide water-ring. If the salt is not much adsorbed, it will spread as far as the water. If a strip of filter-paper be dipped into a solution we get a similar phenomenon; the water will rise much farther than the salt if the latter is adsorbed strongly. Gordon found that with a M/40 CuSO₄ solution the water rose about 9.2 cm in half an hour and the copper salt only 5.5 cm. With a M/2 solution the copper salt rose 9.2 cm and so did the water. Ordinary ink shows the phenomenon well with blotting-paper.

Leighton⁸ has determined the adsorption of caustic soda, hydrochloric acid, sulphuric acid, and phosphoric acid by purified absorbent cotton. These experiments were interesting in two ways. In the first place, they showed that no compounds were formed. In the second place, data were obtained showing the possible error when determining adsorption. The usual method is to shake a known solution with a weighed amount of the adsorbed solid, pipette off some of the supernatant liquid, and

¹ Mem. Chem. Soc., **2**, 399 (1845).

² Jour. prakt. Chem., **83**, 384 (1861).

³ Jour. Chem. Soc., **30**, 662 (1876).

⁴ Ibid., **33**, 304 (1878).

⁵ Chem. News, **51**, 51 (1885).

⁶ Jour. Phys. Chem., **18**, 337 (1914).

⁷ See SAHLBLOM: Kolloidchemische Beihefte, **2**, 79 (1910).

⁸ Jour. Phys. Chem., **20**, 188 (1916).

analyze. The amount of adsorption is calculated from the decrease in concentration. This calculation is accurate only in case no liquid is taken up by the solid adsorbing agent. If the cotton adsorbed the alkali and the water in the same ratio in which they occurred in the solution there would be no change in the concentration of the solution and the apparent adsorption would be zero. To avoid this error, Leighton centrifuged the cotton for an hour in a centrifugal rotating about 4000 revolutions per minute, and then analyzed the cotton. This direct or "gravi-

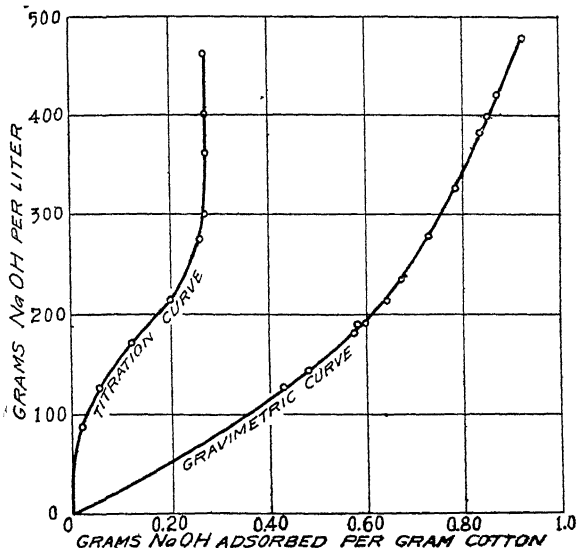


FIG. 5.

metric" method will give too high adsorption unless the centrifuging removes all the unadsorbed solution. On the other hand, the indirect or "titration" method gives too low results unless no water is adsorbed by the cotton at all. Since this last is not true, the results by the titration method are necessarily wrong with cotton, while the results by the gravimetric method may be right. The differences between the two methods may be quite considerable. With a solution of 200 grams NaOH per liter Leighton found an adsorption of 0.27 grams NaOH per gram cotton by the titration method, and of 0.75 gram NaOH by

the gravimetric method. The true adsorption lies between these two values.¹ In Tables XXI-XXIV are given Leighton's data which are also reproduced graphically in Figs. 5-7.

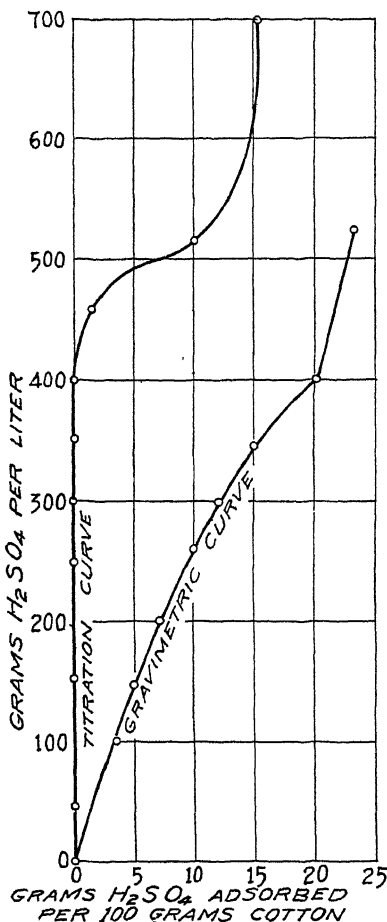


FIG. 6.

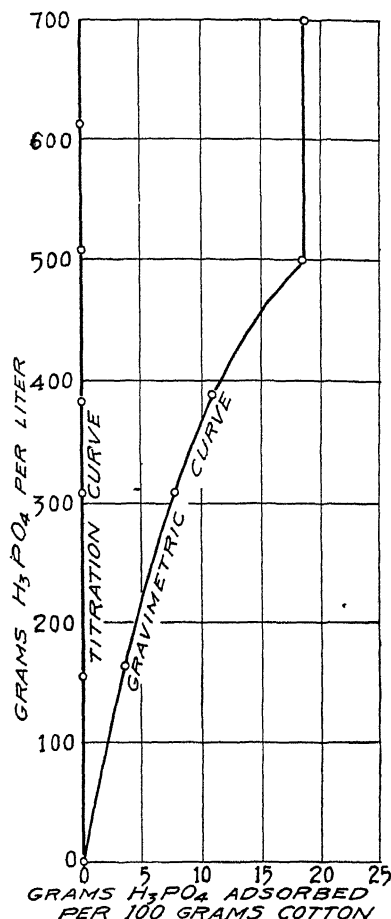


FIG. 7.

Kellner² has studied the adsorption of acids and alkalis by platinum black. One gram of platinum black adsorbed about 20 percent of the hydrochloric acid in 50 cc of a thousandth-

¹ See WEISER and SHERRICK: Jour. Phys. Chem., **23**, 205 (1919).

² Wied. Ann., **57**, 79 (1895).

TABLE XXI.—ADSORPTION OF SODIUM HYDROXIDE BY COTTON

Volume of solution = 100 cc
 Weight of cotton = about 1.0 g.
 Time of run = 3 hours.

Solution grams NaOH per liter	Grams NaOH adsorbed per gram cotton		Solution grams NaOH adsorbed	Grams NaOH adsorbed per gram cotton	
	Gravimetric	Titration		Gravimetric	Titration
474	0 916		230	0 664	
450	.. .	0 28	212	0 662	
427	0 887	..	210	..	0 19
415	0 875	..	190	0 594	
400	..	0 27	189	0 579	
379	0 846		184	0 572	
350	.	0 27	175	0 12
323	0 782		140	..	0 08
300	0 27	138	0 461	
276	0 733	.	125	0 433	
275		0 25	90	.	0 01
231	0 665		40	.. .	0 00

TABLE XXII.—ADSORPTION OF SULPHURIC ACID BY COTTON

Volume of solution = 100 cc.
 Weight of cotton about 1.0 g.
 Time of run = 3 hours.

Solution g H ₂ SO ₄ per liter	Adsorption	
	Gravimetric g H ₂ SO ₄ per 100 g cotton	Titration g H ₂ SO ₄ per 100 g cotton
747 7	2 04
521 7	23 70	1 53
459 2	0 12
413 9	20 99	0 0
352 3	15 36	0 0
302 3	12 55	0 0
252 3	10.00	0 0
202 3	7 35	0 0
151.7	5 77	0 0
101 2	4.65	0 0
50 0	0 0

APPLIED COLLOID CHEMISTRY

TABLE XXIII.—ADSORPTION OF PHOSPHORIC ACID BY COTTON

Volume of solution = 100 cc.

Weight of cotton about 1.0 g.

Time of run = 3 hours.

Solution g H_3PO_4 per liter	Adsorption	
	Gravimetric g H_3PO_4 per 100 g cotton	Titration g H_3PO_4 per 100 g cotton
715.2	18.68	0
514.4	18.43	0
382.9	11.53	0
318.8	8.57	0
158.0	4.53	0

TABLE XXIV.—ADSORPTION OF HYDROCHLORIC ACID BY COTTON

Volume of solution = 100 cc.

Weight of cotton about 1.0 g.

Time of run = 3 hours.

Solution g HCl per liter	Adsorption	
	Gravimetric g HCl per 100 g cotton	Titration g HCl per 100 g cotton
414.0	..	13.97 ¹
373.6	9.1	11.63 ¹
331.3	7.3	9.28 ¹
288.9	6.9	7.00 ¹
209.2	6.2	2.34
114.5	3.1	0
45.8	2.0	

normal solution (about 0.36 mg HCl). The adsorption of caustic potash is greater. The bivalent bases and acids are adsorbed in general more than the univalent ones. Osaka² has made some experiments on the adsorption of potassium and sodium salts by blood charcoal. The charcoal takes up about 85 percent of its weight of water when suspended in saturated water vapor at 25°. If no account is taken of this fact, a very large error

¹ Probably wrong owing to volatilization of HCl.

² Mem. Coll. Sci. Kyoto Univ., **1**, 257 (1915).

may be introduced. When allowance was made for the amount of water adsorbed, it was found that the adsorption with salts of the same base decreased in the order $I > NO_3 > Br > Cl > SO_4$. The results are shown graphically in Fig. 8, the abscissas being milligram equivalents of salt adsorbed per gram charcoal and the ordinates the concentration of the solution in gram equivalents per liter. It will be noticed that potassium salts are adsorbed more strongly than the corresponding sodium salts. The numerical values are given in Table XXV. The percentage adsorptions for normal solutions of KI, KNO_3 , KBr, KCl, and K_2SO_4 are approximately 28, 16, 14, 7, and 5 respectively. Rona and Michaelis¹ find that

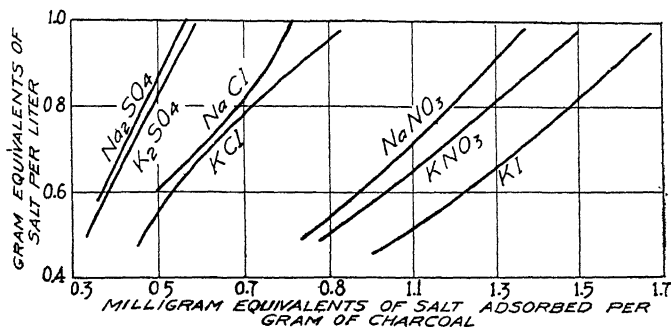


FIG. 8

the order of adsorption of the anions is $OH > CNS > I > NO_3 > Br > Cl > HPO_4 > SO_4$ and of the cations is $H > Al > Cu > Zn > Mg, Ca > NH_4, K, Na$.

With powdered quartz having an estimated surface of 1000 cm^2 per gram, L. J. Briggs² found that 100 grams quartz adsorbed approximately the following amounts for M/10 solutions: NaOH, KOH and NH_4OH , 0.8 millimols; Na_2CO_3 , K_2CO_3 , $(NH_4)_2CO_3$, 0.2 millimols; NH_4Cl , $MgCl_2$, NaCl, $NaNO_3$, Na_2SO_4 , nothing.

An interesting and important case of selective adsorption has been worked out by Lloyd. From fuller's earth he has prepared a hydrous aluminum silicate³ which adsorbs alkaloids. It has been suggested that the material be called Lloyd's reagent.

¹ Biochem. Zeit., **94**, 240 (1919).

² Jour. Phys. Chem., **9**, 623 (1905).

³ WALDBOTT: Jour. Am. Chem. Soc., **35**, 837 (1913).

TABLE XXV.—ADSORPTION OF SALTS BY BLOOD CHARCOAL

Milligrams and milligram equivalents per gram charcoal

Conc. of solution in g equiv / liter	Salt adsorbed by one gram charcoal		Conc. of solution in g equiv / liter	Salt adsorbed by one gram charcoal	
	mg	mg equiv.		mg	mg equiv.
Potassium sulphate			Sodium sulphate		
1.010	51.4	0.59	1.068	40.5	0.57
0.830	45.1	0.52	0.933	37.4	0.53
0.673	37.0	0.42	0.753	31.9	0.45
0.509	29.3	0.34	0.583	25.5	0.36
Potassium chloride			Sodium chloride		
0.966	68.6	0.92	0.998	47.4	0.81
0.765	50.8	0.68	0.896	44.9	0.77
0.562	41.8	0.56	0.697	35.3	0.60
0.470	33.2	0.45	0.597	29.0	0.49
Potassium nitrate			Sodium nitrate		
0.977	151.2	1.50	0.978	116.3	1.37
0.817	129.9	1.28	0.816	107.6	1.27
0.654	112.7	1.11	0.647	99.4	1.03
0.491	87.7	0.87	0.484	69.6	0.82
Potassium iodide			Potassium bromide		
0.967	277.9	1.67	0.970	139.2	1.17
0.833	250.8	1.51	0.717	98.1	0.82
0.622	207.4	1.25	0.526	75.7	0.64
0.464	167.8	1.01			

Carey Lea¹ has shown that silver iodide adsorbs iodine strongly. This property of silver iodide was verified by shaking portions of freshly precipitated and still moist AgI with iodine solutions. An alcoholic solution of iodine, diluted until it has a pale sherry wine color is quickly decolorized by AgI, and the same thing happens with a very dilute solution of iodine in KI, which in a few minutes becomes as colorless as water. It is probably this adsorption which makes silver iodide photographic emulsions apparently less sensitive than the silver bromide emulsions. If so, it should not be difficult to overcome this trouble.

Reinders² has found that when silver chloride crystallizes

¹ Am. Jour. Sci. (3), **33**, 492 (1887).

² Zeit. phys. Chem. **77**, 696 (1911).

from an ammoniacal solution to which gelatine has been added, the crystals contain adsorbed gelatine. This fact is of great importance for the theory of the photographic emulsion. Much other work on adsorption by crystals is to be found in the papers of Marc.¹ The selective nature of the adsorption is shown by the fact that barium sulphate carries down much larger amounts of barium nitrate than of barium chloride.²

In his presidential address before the mathematical and physical section of the British Association, Trouton³ says: "It is a very well known experiment in adsorption to run a solution such as that of permanganate of potash through a filter of sand, or, better, one of precipitated silica, so as to provide a very large surface. The first of the solution to come through the filter has practically lost all its salt owing to have been adsorbed by the surface of the sand.

"I was interested in finding a few months ago that Defoe, the author of Robinson Crusoe, in one of his other books, depicts a party of African travellers as being saved from thirst in a place where the water was charged with alkali by filtering the water through bags of sand. Whether this is a practical thing or not is doubtful, or even if it has ever been tried; for it is only the first part of the liquid to come through the filter which is purified, and very soon the surface has taken up all the salt it can adsorb and after that, of course, the solution comes through intact. It is interesting, however, to know that so long ago as Defoe's time the phenomenon of adsorption from salt solutions had been observed. It is not so well known, that in the case of some salts under the circumstances mentioned above, the first of the solution to come through the sand filter is stronger instead of weaker. This, as already mentioned, is because water, or at least a weaker solution forms the adsorption layer."

On or just back of the beaches at Galveston, Nantucket, and elsewhere, there are wells of fresh water, the levels of which correspond approximately to the ocean level at high tide. It is often believed that the water in these wells comes from the sea and that the salts have been removed in some mysterious

¹ Zeit. phys. Chem., **61**, 385 (1908); **67**, 470; **68**, 104 (1909); **73**, 685 (1910).

² WEISER and SHERRICK: Jour. Phys. Chem., **23**, 205 (1919).

³ Brit. Ass. Reports, **84**, 287 (1914)

way.¹ Unfortunately this is not true. The water comes from inland but is backed up by the ocean and does not flow off so rapidly as it otherwise would. If for any reason the outward flow is checked for a sufficient time, the salt from the ocean does work back into the wells. This has been noticed at Galveston when excessive amounts of water are drawn from the wells.

THE ADSORPTION ISOTHERM

In all cases which have been studied quantitatively the form of the adsorption isotherm is similar to that obtained for the adsorption of gases by solids. Consequently an equation of the same type will represent both sets of phenomena. For solutions we write the equation

$$(x/m)^n = kc$$

where x is the amount adsorbed by m units of the solid adsorbing agent, c is the concentration of the solution, and n is not necessarily an integer though experimentally never less than unity. The approximate accuracy of the formula is shown in Freundlich's data,² Tables XXVI—XXVIII. Other adsorption formulas have been proposed or discussed by Freundlich,³ McBain,⁴ Schmidt,⁵ von Georgievics,⁶ and others;⁷ but no formula is strictly accurate and the simplest one seems the best for the time being. If the curve really runs parallel eventually to the axis of ordinates, the simple formula is necessarily wrong.

That this really does happen seems to be shown very conclusively in some experiments by Schmidt⁸ on the adsorption of acetic acid by charcoal, Table XXIX. The data are plotted in

¹ HILGARD: Soils, 267 (1906).

² Kapillarchemie, 147 (1909); See also VON GEORGIEVICS: Monatsheft für Chemie, **34**, 733 (1913).

³ Zeit. phys. Chem., **57**, 385; **59**, 284 (1907).

⁴ Jour. Chem. Soc., **91**, 1683 (1910).

⁵ Zeit. phys. Chem., **74**, 689 (1910); **77**, 641 (1911); **78**, 667 (1912); **91**, 103 (1916).

⁶ Ibid., **83**, 269 (1914).

⁷ MARC: Zeit. phys. Chem., **81**, 641 (1913); DIETL: Monatsheft für Chemie, **35**, 784 (1914); TRÜMLER: Zeit. Kolloidchemie, **15**, 10 (1914).

⁸ Zeit. phys. Chem., **77**, 650 (1911).

TABLE XXVI.—DISTRIBUTION OF ACETIC ACID BETWEEN WATER AND BLOOD CHARCOAL

$$(x/m)^n = kc.$$

$$n = 2.35; \log k = 0.98.$$

c in mols per liter; x/m in millimols per gram charcoal.

c	x/m found	x/m calc	$\log k$
0 0181	0 467	0 474	0 966
0 0309	0 624	0 623	1.029
0 0616	0 801	0 798	0 984
0 1259	1 11	1.08	1 006
0 2677	1 55	1.49	1 030
0 4711	2 04	1.90	1 055
0 8817	2 48	2 48	0.981
2 785	3 76	4 04	0 906

TABLE XXVII.—DISTRIBUTION OF BROMINE BETWEEN WATER AND BLOOD CHARCOAL

$$(x/m)^n = kc$$

$$n = 2.4; \log k = 0.974$$

c in millimols per liter

x/m in millimols per gram charcoal.

c	x/m found	x/m calc	$\log k$
0.92	2 07	2 09	0 965
2 59	3 10	2 96	1.032
6 69	4 27	4 10	1.028
17 08	5 44	5 64	0.930
29 75	6 80	6 80	0.974

TABLE XXVIII.—DISTRIBUTION OF BENZOIC ACID BETWEEN WATER AND BLOOD CHARCOAL

$$(x/m)^n = kc.$$

$$n = 2.53, \log k = 2.32.$$

c in millimols per liter

x/m in millimols per gram blood charcoal.

c	x/m found	x/m calc	$\log k$
6 18	0.437	0 445	2.299
25 00	0 780	0 776	2.329
53 13	1 04	1.04	2.318
117 73	1 44	1.43	2.330

TABLE XXIX.—ADSORPTION OF ACETIC ACID BY CHARCOAL

100 cc acetic acid solution and 10 grams charcoal.

c_1 = grams acetic acid per 100 cc.

c_2 = grams acetic acid adsorbed.

Sugar charcoal		Animal charcoal	
c_1	c_2	c_1	c_2
0.009	0.052	0.04	0.20
0.032	0.101	0.19	0.49
0.037	0.126	1.20	1.19
0.212	0.322	1.88	1.42
1.16	0.588	3.18	1.68
3.76	0.795	5.09	1.96
3.75	0.811	13.63	2.37
5.60	0.828	14.39	2.47
9.18	0.901	21.52	2.56
12.65	0.953	32.06	2.44
16.60	0.904	38.89	2.50
25.73	0.882		
29.38	0.902		
30.60	0.903		

Fig. 9. In both these cases people who only looked at the last five or six figures might easily decide that a definite compound was formed though it would have to be a different one in each case. If one assumes that the animal charcoal is only 20 per cent carbon, the hypothetical compound would be $C_{20}(CH_3CO_2H)$. By assigning a higher molecular weight to carbon, the formula can be made anything one pleases.

Schmidt¹ does not always give the units which he uses and his manipulation of decimal points is erratic; but he finds that the equation

$$(x/m)^4 = kc$$

represents pretty well the distribution of iodine between charcoal and alcohol or benzene over the range covered by the experiments. For charcoal, water, and acetic acid or succinic acid, the equation takes the form

$$(x/m)^2 = kc$$

¹ *Zet. phys. Chem.*, **15**, 56 (1894).

while the exponent becomes 10 in the case of oxalic acid. For the distribution of potassium chloride between silicic acid and water the exponent is unity, the equation becoming

$$(x/m) = kc$$

The same equation describes the distribution of potassium chloride between stannic oxide and water¹ and between charcoal

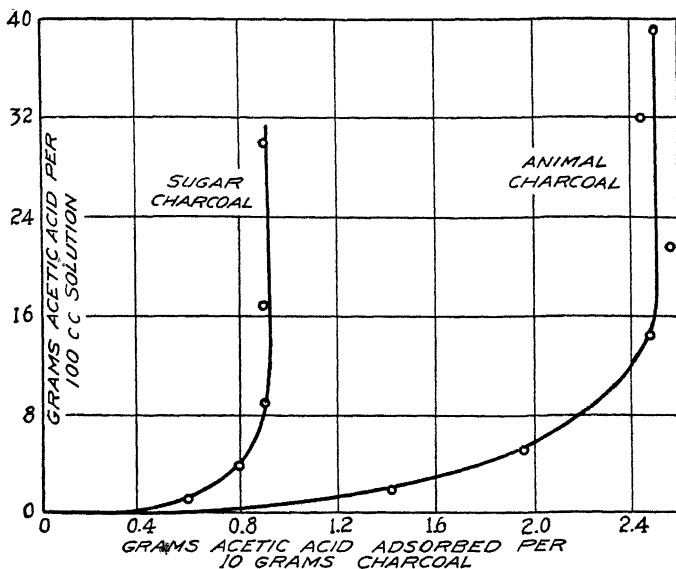


FIG. 9.

and water.² A glance at Fig. 8 shows that Osaka's data for potassium sulphate and potassium nitrate fall very nearly on a straight line and could therefore be given approximately by this equation over the range plotted. This has no special significance because the other data in Fig. 8 distinctly do not give straight lines.

Van Slyke and Van Slyke³ state that the distribution of acids between caseine and water can be represented by the adsorption isotherm, the exponent being 1.95 for sulphuric acid.

¹ VAN BEMMELN: *Zeit. anorg. Chem.*, **23**, 113 (1900).

² LACHS and MICHAELIS: *Zeit. Elektrochemie*, **17**, 2 (1911).

³ *Am. Chem. Jour.*, **38**, 383 (1897).

Georgievics¹ finds that the distribution of indigo;carmine between silk and water and of methylene blue between cellulose and water can be represented by the formula $(x/m)^2 = kc$, while Küster² shows that the distribution of iodine between starch and water can be described by the formula $(x/m)^5 = kc$. Küster's experiments prove that "starch iodide" so-called is not a definite compound. They also furnish a serious objection to the view that the iodine forms a solid solution in starch following the same laws governing the distribution of a substance between two liquid layers. If that were the case the molecular weight of iodine in starch would have to be one-fifth the molecular weight of iodine in water. This means a molecular weight of about 51 for iodine dissolved in starch, which is improbable. This difficulty is avoided when we consider the phenomenon as one of adsorption because there is no known relation between the exponent in the formula for the adsorption isotherm and the molecular weight of anything.

Biltz³ has shown that the blue color obtained when iodine is taken up by basic lanthanum acetate is due to an adsorption of iodine by the salt. The exponential factor is 2. It is 3 for the distribution of alizarine between chromic oxide and water.⁴

Davis⁵ finds that the exponential formula reproduces satisfactorily enough, the data for the distribution of iodine between charcoal and various organic liquids. He considers further that the adsorption of iodine by various charcoals consists of a surface condensation and a diffusion (solid solution) into the interior of the carbon, the surface condensation being nearly instantaneous and quite complete in some hours, while the diffusion proceeds for weeks or months. This conclusion is disputed by Schmidt-Walter,⁶ who believes that the charcoal acted as a catalytic agent causing the iodine to react with the organic liquids.

The adsorption of milk sugar and cane sugar by charcoal has

¹ Sitzungsber. Akad. Wiss. Wien., **103**, IIb, 589 (1894); **104**, IIb, 309 (1895); Zeit. Farbenindustrie, **2**, 253 (1903).

² Liebig's Ann., **283**, 364 (1891).

³ Ber. deutsch. chem. Ges., **37**, 719 (1904).

⁴ BILTZ: Ber. deutsch. chem. Ges., **38**, 4143 (1905).

⁵ Jour. Chem. Soc., **91**, 1666 (1907).

⁶ Zeit. Kolloidchemie, **14**, 242 (1914).

been studied quantitatively by Wiegner,¹ the value of the exponent n being about 4.5 for milk sugar and a little less than 8.2 for cane sugar.

Walker and Appleyard² have studied the very interesting case of picric acid and silk. The distribution of picric acid between silk and water is reversible and can be represented by the equation $(x/m)^{2.7} = kc$. When picric acid is dissolved in dry benzene, however, dry silk does not adsorb any picric acid from the solution, nor does dry silk, dyed with picric acid, lose any picric acid to dry benzene. It is apparently not a case of reversible equilibrium and Walker and Appleyard were unable to account for it. Quite recently a tentative explanation has been put forward³ that picric acid, like many other dyes, exists in two forms: in this case the one colored, the other colorless. In water or alcoholic solution the two forms are in equilibrium, and so reversible equilibrium between the liquid and silk exists. But a carbon tetrachloride solution of picric acid, at least at ordinary temperatures and at 60°, contains so little of the colored modification that reversible equilibrium is reached with difficulty. The case of the benzene solution is complicated by presence of the benzene picric acid compound, but this probably has no dyeing properties. One could also prophesy the same results with ligroin or chloroform solutions—in fact with any colorless solution of picric acid. The effect of solvent on tautomeric change is exemplified in the cases of nitroso-benzene and the pseudonitrols, which as solids are colorless, but yield colored solutions.

Cameron and Patten⁴ find that the distribution of gentian violet between soils and water or of eosine between quartz and water can be represented fairly well by exponential formulas; but that flocculation of the adsorbing medium is apparently a disturbing factor. That flocculation actually does take place had been shown by Patten⁵ in a special set of experiments on quartz flour and dyes.

¹ Zeit. Kolloidchemie, **8**, 126 (1911).

² Jour. Chem. Soc., **69**, 1334 (1896).

³ BLUCHER and FARNAU: Jour. Phys. Chem., **18**, 640 (1914). Cf. STSLEY: Bull. Soc. chim., Paris, 865 (1900).

⁴ Jour. Phys. Chem., **11**, 581 (1907).

⁵ Trans. Am. Electrochem. Soc., **10**, 67 (1906).

In Table XXX are given a list of a few of the systems which have been studied quantitatively. The values for n have undoubtedly been rounded off in most cases.

TABLE XXX.—EXPONENTS IN ADSORPTION ISOTHERMS

Solvent	Solute	Solid	n	Observer
Alcohol	Iodine	Charcoal	4 0	Schmidt ¹
Benzene	Iodine	Charcoal	4 0	Schmidt ¹
Water.	Acetic acid	Charcoal	2 0	Schmidt ¹
Water.. . . .	Succinic acid	Charcoal	2 0	Schmidt ¹
Water.	Oxalic acid	Charcoal	10 0	Schmidt ¹
Water	Potassium chloride	Silicic acid	1 0	Schmidt ¹
Water.. . . .	Potassium chloride	Stannic oxide	1 0	Van Bemme- len ²
Water.... .	Potassium chloride	Charcoal	1 0	Lachs and Mi- chælis ³
Water.. . . .	Sulphuric acid	Caseine	1 95	Van Slyke ⁴
Water.... .	Indigo carmine	Silk	2 0	Georgievics ⁵
Water.... .	Methylene blue	Cellulose	2 0	Georgievics ⁵
Water.	Iodine	Starch	5 0	Kuster ⁶
Water..... .	Alizarine	Chromic oxide	3 0	Biltz ⁷
Water.... .	Milk sugar	Charcoal	4 5	Wagner ⁸
Water.	Cane sugar	Charcoal	8 2	Wagner ⁸
Water.... .	Picric acid	Silk	2.7	Walker and Appleyard ⁹

ABNORMAL ADSORPTION

A still more striking case of flocculation and consequent change of adsorption was studied by Lottermoser and Rothe¹⁰ in the

¹ Zeit. phys. Chem., **15**, 56 (1894).

² Zeit. anorg. Chem., **23**, 113 (1900).

³ Zeit. Elektrochemie, **17**, 2 (1911).

⁴ Am. Chem. Jour., **38**, 383 (1897).

⁵ Sitzungsber. Akad. Wiss. Wien., **103**, IIb, 589 (1894); **104** IIb, 309 (1895); Zeit. Farbenindustrie, **2**, 253 (1903).

⁶ Liebig's Ann., **283**, 264 (1891).

⁷ Ber. deutsch. chem. Ges., **38**, 4143 (1905).

⁸ Zeit. Kolloidchemie, **8**, 126 (1911).

⁹ Jour. Chem. Soc., **69**, 1334 (1896).

¹⁰ Zeit. phys. Chem., **62**, 359 (1908).

adsorption of potassium iodide by silver iodide. For concentrations of potassium iodide in water up to about $M/300$ the exponential formula holds fairly well, the exponential factor being a little over 13. Beyond this concentration the amount of adsorption actually decreases with increasing concentration in the water phase. The change in the structure of the silver iodide can easily be seen under the microscope. The precipitate becomes denser and more granular and shows signs of crystallization. On the other hand silver nitrate is adsorbed by silver iodide without producing this change within the concentrations studied. The exponential factor is 2 for silver nitrate. The silver iodide shows a marked tendency to change in structure and great care is necessary if one wishes to prepare two samples with the same adsorbing power.

Freundlich and Schucht¹ found that amorphous mercuric sulphide changes over spontaneously into a crystalline form and then has a decreased power of adsorbing dyes. The adsorption of eosine by hydrous copper oxide varies with changes in the cupric oxide.² Wagner³ has shown that when the salts of aluminum, iron, etc., are hydrolyzed they adsorb the free acid to some extent; but that in time the adsorption decreases so much that practically all the acid is set free.

Evans⁴ reported a number of cases of apparently abnormal adsorption by filter paper. With hydrochloric acid the amount adsorbed was apparently independent of the concentration of the solution from 0.007N to 0.08N. It then increased to double the amount as the concentration of the solution rose to 0.28N and dropped off apparently to zero with 0.36N HCl with normal acid. In a second series the maximum adsorption was found at about 0.2N HCl and there was apparently no adsorption with N/2 acid. A similar behavior was observed with copper sulphate solutions, the maximum adsorption occurring at about 0.04M CuSO_4 and the adsorption dropping to zero for a 0.13M solution. The case of hydrochloric acid was studied by Miss Murray⁵

¹ *Zeit. phys. Chem.*, **85**, 660 (1913).

² GILBERT: *Jour. Phys. Chem.*, **18**, 592 (1914).

³ *Monatsheft für Chemie*, **34**, 95 (1913).

⁴ *Jour. Phys. Chem.*, **10**, 290 (1906).

⁵ *Ibid.*, **20**, 621 (1916).

who showed that normal results were obtained under ordinary conditions if one titrated with methyl orange as indicator. If one used phenolphthalein as indicator and ignored the presence of carbonate in the standard alkali, abnormal results were obtained. Since the apparently abnormal adsorption in the case of hydrochloric acid was proved to be due to analytical error, it is probable that the measurements with copper sulphate, etc., are not absolutely reliable.

While there is no abnormal adsorption of hydrochloric acid under ordinary conditions, Miss Murray found that the adsorption dropped to less than one-half its original value if filter paper were allowed to stand for 7-10 days in contact with hydrochloric acid solutions. The nature of the change in the filter paper under these conditions is not known. It is also not known whether a similar change is to be observed with purified absorbent cotton.

Biltz and Steiner¹ found abnormal adsorption of night blue and Victoria blue by cotton, the adsorption passing through a maximum with increasing concentration. It is impossible to say to what extent the decreasing adsorption is due to experimental error, to changes in the adsorbing power of the cotton, and to other substances present in the dye-bath.

NEGATIVE ADSORPTION

Lagergren² in 1899, reported the negative adsorption of some chlorides and of ammonium bromide by charcoal, the solution becoming more concentrated after being shaken with the charcoal. Quite recently Osaka³ found that sodium nitrate, potassium bromide, potassium iodide and potassium nitrate are adsorbed positively by blood charcoal while sodium chloride, sodium sulphate and potassium sulphate are apparently adsorbed negatively. The solution of potassium chloride is adsorbed positively when the concentration is comparatively high and is apparently adsorbed negatively when the concentration is comparatively low. With sodium sulphate the increase in concentration was about 1 percent and was less than that with the other salts.

¹ Zeit. Kolloidchemie, **7**, 113 (1910).

² Freundlich: Kapillarchemie, 165 (1909).

³ Mem. Coll. Sci. Kyoto Univ., **1**, 257 (1915).

Mathieu¹ observed negative adsorption with a number of dilute solutions when adsorbed by porous plates, membranes, or capillary tubes. With normal solutions the concentrations in the capillary tubes were often only one-tenth that. The difference in concentration increases with decreasing radius of the capillary tubes and Mathieu considers it quite possible that with very fine tubes water alone would be adsorbed, a conclusion which, as Mathieu himself points out, is of distinct importance for the theory of semi-permeable membranes. If this conclusion is true and general, it accounts for the results of Bigelow² and of Bartell³ who found that osmotic phenomena appeared in porous cups when the pores were sufficiently fine or were clogged sufficiently. It is clear that we can get osmotic phenomena in two distinct ways, depending on whether we have a continuous film or a porous one. In the case of a continuous film, it is essential that the solvent shall dissolve in the membrane and that the solute shall not. Since the permeability is not dependent on adsorption, there is no reason why there should be any fundamental difference between the adsorption of a solute which does pass through the membrane and of one which does not pass through. If we have a porous film, we get osmotic phenomena only in case the pore walls adsorb the pure solvent and the diameter of the pores is so small that the adsorbed film of pure solvent fills the pores full. Under these circumstances the dissolved substance cannot pass through the membrane unless adsorbed by the latter. There is therefore an important difference between a solute which does pass through a porous membrane and one that does not, in that the first is adsorbed by the membrane and the second is not. By making suitable assumptions this distinction can perhaps be eliminated.⁴

Kahlenberg⁵ has shown that benzene, toluene, and pyridine pass through a rubber membrane very readily, while water does not. This is perfectly natural on the assumption that these

¹ Drude's Ann., **9**, 340 (1902).

² Jour. Am. Chem. Soc., **29**, 1576, 1675 (1907); **31**, 1194 (1909).

³ Jour. Phys. Chem., **15**, 659 (1911); **16**, 318 (1912); Jour. Am. Chem. Soc., **36**, 646 (1914); **38**, 1029, 1036 (1916).

⁴ See Tinker: Proc. Roy. Soc., **92A**, 257 (1915).

⁵ Jour. Phys. Chem., **10**, 141 (1906).

liquids dissolve in rubber, but on the basis of pores it is hard to understand why water should not pass through. One might cite the case of the oiled sieve and say that water does not wet rubber, but water does wet rubber. The case of trichloroacetic acid is also interesting. When dissolved in benzene it passes readily through a rubber membrane, whereas it passes very slowly when dissolved in water. This is as it should be if we are dealing with solution, but it is hard to explain if we are dealing with adsorption. While nothing is proved, I am inclined to think that a rubber membrane is not a porous one in the sense that Bartell's clogged plate is, and I believe, therefore, that, when a rubber film acts as a semi-permeable membrane, the solvent dissolves in the rubber and passes through it essentially in that way. There are no satisfactory data in regard to the copper ferrocyanide membrane, but it seems better for the present to consider it as like the rubber membrane.

REVERSIBILITY OF EQUILIBRIUM

To be certain that the equilibrium represented by the adsorption isotherm is a reversible one, it should be reached from both sides. As a rule, that is not done, but Freundlich¹ has made a couple of experiments to show that the same end-point is actually reached. For the distribution of acetic acid between charcoal and water, he obtained a concentration in the water of $N/16.47$ when he shook one gram of charcoal with 100 cc of $N/14.53$ solution, and a concentration of $N/16.49$ when he shook one gram of charcoal with 50 cc of a $N/7.27$ solution and then added 50 cc water. For the distribution of benzoic acid between charcoal and benzene, a similar proceeding with other concentrations gave him the two final values of $N/8.5$ and $N/8.48$. In some cases equilibrium is reached very rapidly from both sides, and in others not.² While the adsorption equilibrium is theoretically a reversible one, there are conditions under which there may be apparent or actual irreversibility. If charcoal takes a dye out of solution to such an extent as to decolorize the water

¹ Kapillarchemie, 148 (1909); see also VON SCHROEDER: Kolloidchemische Beihefte, 1, 14 (1909).

² FREUNDLICH: Zeit. phys. Chem., 57, 388 (1906); OSTWALD: Lehrbuch allgem. Chemie, 1, 1096 (1891); SCHMIDT: Zeit. phys. Chem., 74, 708 (1910).

practically, no amount of washing with water will give a colored solution, even though dye is being taken out all the time.¹ In this case the adsorption is strictly reversible, and the difficulty was in the interpretation of the results.

There is one experiment which I always like to try, because it proves something whichever way it goes. A solution of iodine in water is shaken with bone-black, filtered, and tested with starch paste. If the colorless solution does not turn the starch blue, the experiment shows how completely charcoal extracts iodine from aqueous solution. If the starch turns blue, the experiment shows that the solution, though apparently colorless, still contains iodine which can be detected by means of the sensitive starch test.

If the adsorbing substance changes through agglomeration, crystallization, or in any other way, its specific adsorbing power will change, and the adsorbed substance will be held either more or less firmly, as the case may be. Some instances of this have already been cited under abnormal adsorption. The adsorbed substance may also change on standing or on heating, in which case we shall have an apparent irreversibility, though we are really dealing, as before, with a new reversible equilibrium. This case occurs very frequently in dyeing.²

SPECIFICITY OF ADSORPTION

Since adsorption is essentially specific, the amount of adsorption will necessarily vary with the nature of the adsorbing agent, the liquid, and the substance to be adsorbed. In illustration of this, Freundlich³ cites the experiments of Wöhler, Pluddeman and Wöhler⁴ to the effect that charcoal and ferric oxide adsorb benzoic acid about ten times as strongly as acetic acid, while chromium oxide adsorbs the two acids about equally, and platinum black adsorbs acetic acid a little, but benzoic acid practically not at all. All salts seem to show distinct adsorption for their own ions. Thus silver bromide adsorbs silver nitrate or potas-

¹ FREUNDLICH and NEUMANN: *Zeit. phys. Chem.*, **67**, 538 (1900).

² LAKE: *Jour. Phys. Chem.*, **20**, 761 (1916).

³ *Kapillarchemie*, 155 (1909).

⁴ *Zeit. phys. Chem.*, **62**, 664 (1908).

sium bromide, but not potassium nitrate. Charcoal adsorbs both acid and basic dyes. Alumina takes up many acid dyes readily and not the basic dyes: silica and tannin adsorb the basic dyes more readily than acid dyes. Wool adsorbs many dyes strongly without a mordant and cotton relatively few. What is known as Schulze's law¹ is that the power of active ions to precipitate colloidal solutions is a function of their valence, or of the number of electrical charges which they carry. Since the precipitating power, in the cases studied by Schulze, depends on the degree of adsorption, it follows that, in so far as Schulze's law holds, a trivalent ion will be adsorbed more strongly than a bivalent ion, and the latter more strongly than a univalent one. Schulze's law is merely a first approximation. Everybody recognizes that hydrogen and hydroxyl ions are not to be classed with the other univalent ions, because they are usually adsorbed much more strongly,² and everybody recognizes that there are other exceptions. In case of doubt, it is generally safe to assume that an ion of higher valence will be adsorbed more strongly than one of lower valence, but it is a mistake to consider this so-called law as anything more than a guide. For instance, Osaka³ found that charcoal adsorbed potassium salts in the following order when the salts were present in equivalent concentrations: $KI > KNO_3 > KBr > KCl > K_2SO_4$, from which it follows, that, for equivalent concentrations, the sulphate ion is adsorbed the least of all. If we were to compare molecular concentrations the sulphate ion would be adsorbed as strongly as the bromide ion, but less than the nitrate or the iodide ion. Davis⁴ found that the order of adsorption of iodine from different liquids was not the same with different kinds of charcoal. With animal charcoal there was decreasing adsorption in the order: chloroform, alcohol, ethyl acetate, benzene, and toluene; with sugar charcoal the adsorption decreased in the order: chloroform, toluene, ethyl acetate, benzene, and alcohol; whereas for cocoanut charcoal the order was toluene, chloroform, benzene, alcohol, and ethyl acetate. There are at least two factors governing the effect of

¹ SCHULZE: Jour. prakt. Chem. (2) **25**, 43 (1882); **27**, 320 (1884).

² FREUNDLICH: Kapillarchemie, 354 (1909).

³ OSAKA: Mem. Coll. Sci., Kyoto, **1**, 267 (1915).

⁴ Jour. Chem. Soc., **91**, 1682 (1907).

the solvent. The more soluble the dissolved substance is in a given solvent, the less readily will it be adsorbed, provided we can neglect the adsorption of the solvent itself by the solid. There are many illustrations of this, but one will suffice. Charcoal will decolorize aqueous solutions of iodine or of methyl violet, but alcohol will extract the color from the charcoal. The solubility cannot be the sole factor, however, because then the solvents could always be arranged in the same order for the same solute, regardless of the nature of the adsorbing agent. This is disproved absolutely by the experiments of Davis. One other factor is the adsorption of the solvent by the adsorbing agent. This factor was not taken into account at all by Davis, whose data are therefore not sufficient to enable us to tell whether there are other factors to be considered.

In so far as adsorption is accompanied by an evolution of heat, the amount of adsorption must decrease with rising temperature. This is found to be the case experimentally, but the change is often a very small one. In some cases there is an apparently large increase in adsorption with rising temperature. Thus wool takes up very little acid violet at 20° and a great deal at about 95°. Experiments showed¹ that this adsorption is not reversible, for the acid violet adsorbed at the higher temperature cannot be washed out to any extent at 20°. After adsorption the dye agglomerates or changes so that it becomes practically insoluble and consequently the wool takes up more dye.

ADSORPTION OF SEVERAL SOLUTES

Some years ago there was a widespread rumor that strychnine had been added to a certain breakfast cereal to make it more appetizing. The report was false and not even new, for in 1852 it was alleged that strychnine was being added to certain English pale ales. In order to show that strychnine could be detected in beer if present, Graham and Hofmann² shook two ounces of animal charcoal with half a gallon of beer to which 1/2 grain of strychnine had been added. The strychnine was removed practically completely by the charcoal, and was extracted from that with alcohol and identified.

¹ LAKE: Jour. Phys. Chem., 20, 761 (1916).

² Jour. Chem. Soc., 5, 713 (1853).

Skey¹ reports that dilute sulphuric acid can be freed from traces of nitric acid by shaking with charcoal, while concentrated sulphuric acid cannot be. Dudley² showed that the rank and disagreeable odor of raw whiskey can be removed by leaching through charcoal. Schmidt³ has studied the simultaneous adsorption of iodine and acetic acid by charcoal from solution in water and in ethyl acetate. With both solvents less of each substance was adsorbed than if the other had not been present. Schmidt believes that this is general, but this statement is undoubtedly too broad, though it holds in many cases. Freundlich and Masius⁴ studied the adsorption of pairs of organic acids and obtained results similar to those of Schmidt. They also found that the acid, which is adsorbed more, is displaced less when the two acids are present in the solution. These experiments throw light on Skey's experiments. With increasing relative concentration of sulphuric acid, we should expect an increasing displacement of nitric acid from the charcoal, which is what actually occurred. Lachs and Michaelis⁵ found that caustic potash cut down very much the adsorption of potassium chloride by charcoal from water. In other words, the presence of the strongly adsorbed hydroxyl ion decreased the adsorption of the chloride very much. They also found that if sulphuric acid is added in small amounts to the chloride solution the adsorption of chloride ion is increased markedly. This is in accord with the results of Osaka,⁶ that potassium chloride is adsorbed more than potassium sulphate, or sodium sulphate, and, presumably, hydrochloric acid more than sulphuric acid.

Thorium salts cut down the adsorption of uranium X by charcoal⁷ and acetone and acetic acid decrease the adsorption of grape-sugar by charcoal⁸ but albumin and acetone have no effect

¹ Chem. News, **17**, 217 (1886).

² Jour. Am. Chem. Soc., **30**, 1784 (1908).

³ Zeit. phys. Chem., **74**, 730 (1910).

⁴ Van Bemmelen Gedenkboek, 88 (1910).

⁵ Zeit. Elektrochemie, **17**, 1 (1911).

⁶ Mem. Coll. Sci. Kyoto Univ., **1**, 267 (1915).

⁷ FREUNDLICH and KAEMPFER: Zeit. phys. Chem., **90**, 681 (1915).

⁸ RONA and MICHAELIS: Biochem. Zeit., **16**, 499 (1909).

ADSORPTION FROM SOLUTION

on each other, nor does one acid dye apparently displace another on wool or silk.¹

If we have two salts with no common ion, it is easy to see that the most strongly adsorbed cation and anion will be taken up the most, while the other pair will be adsorbed the least readily. In the case of dyeing we have an admirable illustration of the fact, first recognized by Lachs and Michaelis,² and by Estrup,³ that an anion is adsorbed more readily in presence of a readily adsorbed cation and a cation in presence of a readily adsorbed anion. In an acid dye the color is in the acid radical and in a basic dye the color is in the basic radical. An acid dye will therefore be taken up more strongly in an acid solution than in a neutral solution and will be taken up least in an alkaline solution. A readily adsorbed anion will decrease the amount of dye taken up and a readily adsorbed cation will increase it. With a basic dye the reverse will be true. The dye will be taken up most readily in an alkaline solution but may be taken up in a natural or acid solution. A readily adsorbed cation will cut down the adsorption of the dye and a readily adsorbed anion will increase it.

In Tables XXXI-XXXII are data by Pelet-Jolivet⁴ for crystal ponceau, an acid dye.

TABLE XXXI.—ADSORPTION OF CRYSTAL PONCEAU BY WOOL

Volume of solution = 200 cc.

Weight of wool = 5 grams.

x = percent crystal ponceau.

x	Milligrams crystal ponceau adsorbed		
	3 cc N/10 H ₂ SO ₄	Water	0.12 g Na ₂ SO ₄
0.1	65	41 7	36.2
0.2	113	62 8	59.8
0.3	150	76 5	64.8
0.4	178	86 5	70 8

¹ LAKE: *Jour. Phys. Chem.*, **20**, 751 (1916).

² *Zeit. Elektrochemie*, **17**, 1 (1911).

³ *Zeit. Kolloidchemie*, **11**, 8 (1912).

⁴ *Die Theorie des Farbeprozesses*, **94**, 149 (1910).

APPLIED COLLOID CHEMISTRY

TABLE XXXII.—ADSORPTION OF CRYSTAL PONCEAU BY WOOL

Volume of solution = 200 cc.

Weight of wool = 5 grams.

Crystal ponceau = 0.372 mg.

cc N/10 acid added	Milligrams crystal ponceau adsorbed		
	HCl	H ₂ SO ₄	H ₃ PO ₄
0	44	42	42
8	109	93	48
18	158	140	80
28	171	153	102

In acid solution crystal ponceau is adsorbed more strongly than in a water solution, while the presence of the strongly adsorbed anion of sodium sulphate cuts down the adsorption over that in water. In the acid solution the strongly adsorbed phosphate anion works against the strongly adsorbed hydrogen cation and consequently the dye is least adsorbed in a phosphoric acid solution and most adsorbed in a hydrochloric acid solution.

In Tables XXXIII and XXXIV are data by Pelet-Jolivet¹

TABLE XXXIII.—ADSORPTION OF METHYLENE BLUE BY SILK AND COTTON

A = 0.3 gram silk in 50 cc 0.2 percent methylene blue.

B = 3 grams cotton in 100 cc 0.1 percent methylene blue.

Fiber	Methylene blue adsorbed, mg		
	2 cc N/10 HCl	Neutral solution	2 cc N/10 KOH
Silk (A)	1 3	10 8	40 6
Cotton (B)	1 2	11 2	30.0

for methylene blue, a basic dye. The most dye is taken up in the alkaline solution and the least in the acid solution which is just as it should be. For the same concentration of acid, more dye is taken up in a phosphate solution than in a sulphate solution while still less is adsorbed from a hydrochloric acid solution; and we should expect the phosphate radical to be adsorbed the

¹Die Theorie des Farbeprozesses, 95 (1910).

ADSORPTION FROM SOLUTION

most and the chlorine radical the least. This comparison is not strictly accurate because equivalent concentrations of two acids do not necessarily mean equal degrees of acidity. On the other hand the amount of hydrogen as ion in 20 cc N/10 H₂SO₄

TABLE XXXIV.—ADSORPTION OF METHYLENE BLUE BY WOOL

Volume of solution = 200 cc.

Weight of wool = 3 grams.

Concentration of methylene blue = 0.8 percent

Acid added	Methylene blue adsorbed, mg		
	N/10 HCl	N/10 H ₂ SO ₄	N/10 H ₃ PO ₄
0	156	156	152
10	22	37	79
20	20	27	32
30	17		

is unquestionably greater than in 10 cc N/10 HCl after both have been diluted to 200 cc, and, yet, more methylene blue is taken up in this sulphuric acid solution than in the hydrochloric acid solution. The difficulty in regard to the acidity can be got round by adding salts. Some data¹ are given in Table XXXV. At

TABLE XXXV.—ADSORPTION OF METHYLENE BLUE BY WOOL

Volume of solution = 100 cc

Weight of wool = 1 gram.

Methylene blue in solution, percent	Methylene blue adsorbed, mg		
	No salt	0.06 g Na ₂ SO ₄	0.06 g Na ₂ HPO ₄
0.1	35	45.6	81.1
0.2	40	52.2	91.3
0.3	43	56.4	95.6
0.4	44	59.4	98.6

every concentration of dye more dye is fixed in the bath containing sulphate than in the bath to which no salt is added, while still more dye is adsorbed in the phosphate solution. We see

¹ Pelet-Jolivet: Die Theorie des Farbeprozesses, 118 (1910).

thus the amount of adsorption varying in the order $\text{Na}_2\text{HPO}_4 > \text{Na}_2\text{SO}_4 > \text{NaCl} > \text{H}_2\text{O}$. Just as should be the case, sodium sulphate increases the amount of a basic dye taken up, whereas it decreases the amount of an acid dye adsorbed. With 0.5 gram silk in 50 cc 0.2 percent methylene blue solution, the amounts of methylene blue taken up were 28.6, 18.4, 13.3, and 10.8 mg when sodium phosphate, sodium sulphate, sodium chloride, and nothing were added respectively to the solution.¹ With cotton there was no difference under the same circumstances; but there was a marked difference when the cotton had been treated with tannin. The effect of different cations was also studied by Pelet-Jolivet who found that silk took up 13.3 mg methylene blue from a solution containing sodium chloride and only 6.3 mg from a solution containing barium chloride, the strongly adsorbed barium cation thus cutting down the adsorption of the basic dye. With wool the depth of color decreases in the following order: sodium phosphate, sodium sulphate, no addition, barium chloride, and platinum tetrachloride. Cotton takes up less methylene blue from a solution containing barium chloride than from one containing sodium chloride.

With substantive dyes the effects of electrolytes are different because these dyes are in colloidal solution and the question of stability enters in. Abnormal results are also to be expected with acid and basic dyes which form colloidal solutions.

When an acid dye is adsorbed nearly completely by the fiber it may easily happen that the differences between acids becomes so small as to be practically negligible.² The concentration of the anion can be increased very much relatively to the concentration of hydrogen as ion by adding salt, and thus the effect of the anion can be brought out. This is shown in Table XXXVI. In the third column are given the amounts of dye adsorbed when acids alone are added to the bath. In the fifth column are the amounts of dye adsorbed when the solution contains 10 cc N/10 acid + 10 cc N/1 salt. With the acids alone the amount of adsorption of acid violet is practically independent of the nature of the acid. With croceine orange, sulphuric acid and phosphoric acid behave practically alike and cut down the adsorption as compared with

¹ PELET-JOLIVET: *Die Theorie des Färbeprozesses*, 118 (1910).

² LAKE: *Jour. Phys. Chem.*, **20**, 785 (1916).

ADSORPTION FROM SOLUTION

hydrochloric acid. With acid violet the addition of sodium chloride has no appreciable effect. The slight apparent increase in adsorption is probably due to experimental error. With croceine orange the sodium chloride cuts down the adsorption slightly. With sodium phosphate the effect is quite extraordinary,

TABLE XXXVI.—ADSORPTION OF ACID VIOLET AND CROCEINE ORANGE BY WOOL

Volume of solution = 250 cc.

Weight of wool = 1 gm.

Amount of dye = 40 mg.

Temperature = 100°.

Time of run = 1 hr.

Acid dye	10 cc N/10 acid	Adsorbed dye, mg	Acid + 10 cc N/1 salt	Adsorbed dye, mg
Acid violet	HCl	39.2	NaCl	39.5
	H ₂ SO ₄	39.2	Na ₂ SO ₄	36.8
	H ₃ PO ₄	39.1	Na ₂ HPO ₄	1.0 ¹
Croceine orange	HCl	38.0	NaCl	33.4
	H ₂ SO ₄	35.5	Na ₂ SO ₄	20.0
	H ₃ PO ₄	35.5	Na ₂ HPO ₄	0.1 ¹

the adsorption of acid violet and of croceine orange being cut almost to zero. The change in the hydrogen ion concentration cannot account for this because 38 mg acid violet and 32 mg croceine orange are adsorbed from a water solution under similar circumstances. We are therefore dealing with a specific effect of the phosphate radical.

Qualitative experiments along the same lines have been obtained by Davison.² With acid green and emerald green on wool and with fast green and safranin on cotton, good illustrations are obtained of the generalization that acid dyes are taken up more completely in an acid solution than in a neutral one and least of all in an alkaline solution, while the reverse is true with basic dyes. Marked differences between the dyeing in acid and alkaline solutions can be obtained on wool with fast green, fast blue, acid violet, croceine orange, crystal ponceau, chrysoidine, safranin, and methylene blue; on cotton with

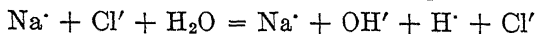
¹ These experiments are probably not strictly comparable with the others owing to the change in hydrogen ion concentration.

² Jour. Phys. Chem., 17, 737 (1913).

acid violet, croceine orange, and emerald green. The generalization that addition of sodium sulphate cuts down the adsorption of acid dyes and increases the adsorption of basic dyes is shown excellently on wool with acid green, fast blue, croceine orange, Victoria blue, chrysoidine, and safranine; on cotton with benzo-purpurine. The effect of continuously varying concentrations of sodium sulphate is shown well on wool with brilliant blue and safranine; on cotton with safranine. When alumina is precipitated from an aluminum acetate solution, it adsorbs fast green, acid green, and croceine orange considerably; but when precipitated from an aluminum sulphate solution it carries down practically no fast green, acid green, or croceine orange. The presence of sulphate decreases the adsorption of acid dyes by alumina as well as by wool. Another illustration of this is that alumina precipitated from an aluminum sulphate solution can only decolorize dilute solutions of alizarine, alizarine green, benzo orange, coeruleine, and acid violet, while alumina precipitated from an acetate solution will decolorize more concentrated solutions. In these experiments with alumina the dye was added to the solution before the alumina was precipitated. It seems probable that if alumina were precipitated from a sulphate solution with barium hydroxide or calcium hydroxide, the effect due to the sulphate would disappear owing to the insolubility of the barium or calcium sulphate. This experiment was not tried.

CHEMICAL ACTION

Selective adsorption connotes the possibility of chemical decomposition as a result of adsorption. If a given substance adsorbs a base more strongly than an acid for instance, there will be a tendency for the salt of that base and that acid to hydrolyze, the base being then adsorbed to a greater extent than the acid. Theoretically there is always some hydrolysis even with sodium chloride and water according to the equation



but this reaction does not run far because caustic soda and hydrochloric acid are strong electrolytes and we cannot have a high simultaneous concentration of hydrogen and hydroxyl as ions. If the caustic soda is removed by adsorption, the hydrolysis can go farther. How complete the hydrolysis will be

depends on the degree to which the base is adsorbed and on the strength of the acid. Any acid will tend to react with adsorbed caustic soda; but that tendency will be greater the stronger the acid. We thus see that a neutral solution will become acid if shaken with a substance which adsorbs the base much more strongly than the acid, that it will become alkaline if the substance adsorbs the acid much more strongly than the base, and that it will remain neutral in case the solid does not adsorb either base or acid at all, or in case it adsorbs the two in practically equivalent amounts either separately or as undissociated salt. The amount of base or of acid taken up from a salt solution will be greater the weaker the unadsorbed acid or base. Many cases are known where the solution does become acid or alkaline when shaken with an adsorbing agent and this has nothing to do with any hypothetical acidity or alkalinity of the adsorbing substance.

If fuller's earth be shaken with water and then filtered, the filtrate is neutral to litmus paper¹ or to phenolphthalein, showing that no soluble base or acid is present. If fuller's earth be shaken with a sodium chloride solution and filtered, the filtrate is acid to litmus or to phenolphthalein. This is because fuller's earth has adsorbed the base. If one presses litmus paper against moistened fuller's earth, the litmus paper turns red, and if one adds fuller's earth to a faintly alkaline solution of phenolphthalein, the red color disappears. This is not because the fuller's earth is acid, but because it takes the base from the sodium chloride, the litmus, or the phenolphthalein.

I have been told that the adsorbing power of fuller's earth is so great that an acre-foot of soil would adsorb 30,000 lb. of lime and that this would make fuller's earth about equivalent in acidity to a two percent sulphuric acid solution.

Silk has such a marked selective adsorption for rosaniline (magenta) that it will not only decompose the hydrochloride, leaving the acid behind, but will also convert the carbinol base back into the color base in presence of an excess of ammonia,² the silk being dyed red from a colorless ammoniacal solution.

¹ Cf. CAMERON: *Jour. Phys. Chem.*, **14**, 400 (1910).

² JACQUEMIN: *Comptes rendus*, **82**, 261 (1876); see also MILLS: *Jour. Chem. Soc.*, **35**, 27 (1879); FORTUYN: *Zeit. phys. Chem.*, **90**, 236 (1915.)

This is the more remarkable because the free color base is unstable and cannot be isolated in a pure state. This makes it seem certain that silk stabilizes the free color base. Another similar instance is the mordanting of wool with copper salts, coloring it green. This green does not change to black when the wool is heated to boiling, though hydrous copper oxide by itself changes very readily. Blucher and Farnau¹ have extended Tommasi's² experiments on the stabilization of hydrous copper oxide by manganese salts and find that a number of other metallic hydroxides are also effective. Bayliss³ has obtained results, which indicate that alumina stabilizes the free acid of Congo red, and Schaposchnikoff and Bogojawlenski⁴ have isolated this metastable form by allowing the pyridine salt to effloresce. Passive iron is an unstable oxide, presumably FeO_2 or FeO_3 , stabilized when adsorbed by metallic iron.⁵

When discussing the adsorption of gases by solids, numerous instances were given of so-called contact catalysis. With solutions the effect of contact materials is as yet relatively unimportant. Lassar-Cohn⁶ gives a few instances where yields have been increased by the use of porous masses. When two parts of acetanilide were heated with one part of zinc chloride, a yield of 3.5 percent flavaniline hydrochloride was obtained. In presence of two parts of infusorial earth the yield increased to about 7.5 percent. When benzene and chloroform react in presence of aluminum bromide, the yield increases from 33 percent to 44 percent when infusorial earth is added. The sulphonation of benzene, xylene, naphthalene, anthraquinone, aniline, etc., is simplified very much by the addition of infusorial earth or of charcoal. When α -dinitronaphthalene is treated with sulphuric acid under suitable conditions in presence of infusorial earth or charcoal, oxidation takes place with elimination of the nitro groups and formation of naphthazarin.

¹ Jour. Phys. Chem., **18**, 629 (1914).

² TOMMASI: Bull. Soc. chim. Paris (2) **37**, 197 (1882); Comptes rendus **99**, 37 (1884).

³ Proc. Roy. Soc., **84B**, 881 (1911).

⁴ Jour. Russ. Phys. Chem. Soc. **44**, 1813 (1913).

⁵ BENNETT and BURNHAM: Jour. Phys. Chem., **21**, 107 (1917).

⁶ Arbeitsmethoden für organisch-chemische Laboratorien, 584, 72, 1079, 923 (1903).

Gurwitsch¹ reports that amylene polymerizes readily on standing in contact with "floridin," which is a hydrous silicate of some sort. Playfair² found that a solution of nitric acid could be prepared which would only bleach a piece of cloth dyed with indigo when the cloth was in contact with alumina, chromic oxide, or stannic oxide. Richardson³ believes that petroleum and bitumens are formed by the polymerizing or condensing action of clays or sands.

A case which has been studied a great deal quantitatively is the decomposition of hydrogen peroxide solutions by platinum. One of the most interesting things about this reaction is its extreme sensitiveness to so-called poisons.⁴ The rate of decomposition of hydrogen peroxide by a given solution of colloidal platinum was reduced approximately to one-half by $M/20,000,000$ HCN, $M/2,000,000$ $HgCl_2$, and $M/300,000$ H_2S . Curiously enough the catalytic action of platinum and of ferments on hydrogen peroxide is decreased in both cases by very slight traces of poisons, such as prussic acid, hydrogen sulphide, etc. It has also been shown by Schönbein⁵ that these same substances cut down the catalytic action of red blood corpuscles on hydrogen peroxide.

In Table XXXVII are given data⁶ for the concentrations necessary to cut down the rate of decomposition of hydrogen peroxide to one-half in the case of colloidal platinum and of haemase, the active enzyme in the red blood corpuscles. While many of the substances that cut down the platinum catalysis also decrease the catalytic action of haemase, there are many cases where no parallelism occurs. Thus carbon monoxide is very toxic to platinum and has no effect on haemase. On the other hand, nitric acid, sulphuric acid, potassium nitrate, and potassium chlorate have practically no effect on platinum and are quite toxic to haemase. Even where there is a general parallelism, one must not follow it too closely. With platinum the prussic acid solution

¹ Zeit. Kolloidchemie, **11**, 18 (1912).

² Mem. Chem. Soc. **3**, 354 (1847).

³ Jour. Ind. Eng. Chem., **8**, 4 (1916); Met. Chem. Eng., **16**, 25 (1917).

⁴ BREDIG and VON BERNECK: Zeit. phys. Chem., **31**, 258 (1899); BREDIG and IKEDA: Ibid., **37**, 1 (1901).

⁵ Jour. prakt. Chem., **105**, 202 (1868).

⁶ SENTER: Zeit. phys. Chem., **51**, 701 (1905).

has one-tenth the concentration of the mercuric chloride solution, while with haemase it has double the concentration. The tabulated concentration for mercuric chloride is the same for platinum as for haemase, while that of iodine dissolved in potassium iodide is one hundred times as great for haemase. Kastle and Loevenhart¹ point out that prussic acid is a strong poison for colloidal

TABLE XXXVII.—THE POISONING OF COLLOIDAL PLATINUM AND HAEMASE

Concentrations at which poisons reduce the rate of the catalytic decomposition of hydrogen peroxide approximately to one-half.

Poison	Colloidal platinum	Haemase
H ₂ S ..	M/300,000	M/1,000,000
HCN.. . . .	M/20,000,000	M/1,000,000
HgCl ₂	M/2,000,000	M/2,000,000
HgBr ₂	M/300,000
Hg(CN) ₂	M/200,000	M/300,000
I ₂ in KI	M/5,000,000	M/50,000
NH ₂ OH HCl	M/25,000	M/80,000
Phenyl hydrazine	M/20,000
Aniline.....	M/5,000	M/400
Arsenious acid	M/50	No poisoning at M/2,000
CO...	Very poisonous	No poisoning
HCl	M/3,000	M/100,000
NH ₄ Cl.	M/200	M/1,000
HNO ₃	No poisoning	M/250,000
H ₂ SO ₄	No poisoning	M/50,000
KNO ₃	No poisoning	M/40,000 at 0°
KClO ₃	Slight poisoning?	M/40,000 at 0°

platinum and silver but accelerates the catalysis of hydrogen peroxide by iron and copper.

It seems probable that the poisons are adsorbed strongly by the catalytic agent and therefore prevent the adsorption of hydrogen peroxide.² This adsorption will be specific and will therefore in general not be the same quantitatively for different catalytic agents. On the other hand, there may well be a qualitative agreement in some or even in many cases. Owing to the extreme

¹ Am. Chem. Jour., **29**, 397 (1903).

² Cf. SENTER: Zeit. phys. Chem., **51**, 702 (1905); DENHAM: Ibid., **72**, 689 (1910).

flexibility of this hypothesis there is nothing as yet to prevent its accounting for all the phenomena observed.¹ On the other hand it must be remembered that proof is still lacking that platinum adsorbs prussic acid for instance, very much more strongly than hydrogen sulphide, and that there is no difference with haemase. There may be other factors which must be taken into account. Thus Bredig² points out that when colloidal platinum is allowed to stand in contact with hydrogen peroxide and concentrated potassium cyanide, the platinum flocculates and precipitates. The agglomerated platinum causes the hydrogen peroxide to decompose, thus showing that the cyanide does not poison precipitated platinum black. There seem to be only two possible explanations. One is that the adsorption of potassium cyanide by platinum falls off very much more rapidly with increasing size of the platinum particles than the adsorption of hydrogen peroxide by platinum. The other explanation is that, through oxidation or otherwise, there is formed what might be called an anti-body, which cuts down the adsorption of the cyanide. Neither hypothesis is very satisfactory and there is no experimental evidence for either, except that Jablczynski³ found that platinized platinum decomposes chromous chloride three times as fast and hydrogen peroxide one hundred times as fast as does smooth platinum foil. The matter should be taken up because Rosnyak⁴ claims that the catalytic action of platinum on hydrogen peroxide decreases with increasing dispersity of the platinum and Felgate⁵ states that pulverulent nickel reduces nitric oxide while colloidal nickel does not. In both these cases it is probable that some factor has been overlooked or not stated. The more finely divided the platinum the more likely the surface is to be coated with oxide and it does not follow at all that the catalytic action of metallic platinum is the same as that of an oxide of platinum. If platinum is kept in suspension by means of gelatine or some similar substances, this will have an effect on the adsorption and the catalytic action.

¹ Cf. FREUNDLICH and KAEMPFER: *Zeit. phys. Chem.*, **90**, 681 (1915).

² *Zeit. phys. Chem.*, **31**, 332 (1899).

³ *Ibid.*, **64**, 751 (1908).

⁴ *Ibid.*, **85**, 68 (1913).

⁵ *Chem. News*, **108**, 178 (1913).

A comparatively recent technical development in contact catalysis is the hardening of oils, by the conversion of oleic acid or olein, for instance, into stearic acid or stearin by the action of hydrogen on the liquid unsaturated oil in presence of a suitable catalytic agent.¹ In 1908 Paal² proposed using a colloidal metal as the catalytic agent at ordinary temperatures. Colloidal solutions of platinum, palladium, osmium, and iridium have been made, of which the palladium hydrosol appears to possess the greatest value. When hydrogen at ordinary temperatures is passed into glycerides of the unsaturated fatty acid to which some palladium hydrosol has been added, reduction takes place. It is more satisfactory, however, to precipitate the metal on an inert base such as magnesia or kieselguhr.

A cheaper and apparently better method is to use nickel as a catalytic agent for the hydrogenation of liquid, unsaturated acids, the reduction taking place at about 250°–300°. There has been some controversy whether the catalytic agent was really metallic nickel³ or an unspecified oxide or oxyhydride;⁴ but there seems to be little doubt but that the metal is the catalytic agent. Some details in regard to the preparation of the catalytic agent are given by Ellis.⁵ Paal and Karl⁶ report that the oxides of lead, cadmium, zinc, aluminum and iron cut down the catalytic action of palladium, while the oxides of magnesium, nickel, and cobalt do not.

ADSORPTION FROM SOLUTION BY LIQUID

There is no reason why there should not be adsorption by a liquid just as well as by a solid, except that the matter is complicated by the possibility of the solute dissolving in the second

¹ COPLING: *Catalysis and its Industrial Applications*, 65, 75 (1916).

² Ber. deutsch. chem. Ges., **41**, 2282 (1908).

³ MEIGEN: Jour. prakt. Chem. (2) **92**, 390 (1915).

⁴ BEDFORD and ERDMANN: Jour. prakt. Chem. (2) **87**, 425 (1913); SIEGMUND and SAIDA: Ibid. (2) **91**, 442 (1915); ERDMANN: Ibid. (2) **91**, 469 (1915); GLASER: Zeit. anorg. Chem., **36**, 1(1903); BELLACCI and CORELLI: Ibid., **86**, 88 (1914); SABATIER and ESPIL: Comptes rendus, **158**, 568; **159**, 137 (1914).

⁵ Jour. Soc. Chem. Ind., **31**, 1163 (1912); *The Hydrogenation of Oils*, 2d. Ed., 108 (1918).

⁶ Ber. deutsch. chem. Ges., **46**, 3069 (1913).

ADSORPTION FROM SOLUTION

liquid. An interesting case of such adsorption was studied by Wilson,¹ Swan,² and Twomey.³ When a drop of chloroform or carbon tetrachloride is placed on the bottom of a glass dish and water or dilute acid poured over it, the drop is well rounded. If the solution is made alkaline, the drop flattens out. The flattening is clearly not due to a change in surface tension of the water phase, because Wilson found that the effect of alkali was the same qualitatively whether sodium chloride was present or not, whereas the addition of salt increases the surface tension of the water phase. What happens is that hydroxyl is adsorbed at the dimeric interface, lowering the surface tension and causing the organic liquid to flatten. This is confirmed by the experiments of von Lerch⁴ who determined the surface tension between benzene and water by means of the rise in capillary tubes.⁵ The surface tension between pure benzene and pure water was found to be 32.6 dynes/cm at 15°-16°. With M/4 NaOH the value dropped to 20.7 and with M/2 NH₄OH to 27.3. The lowering of the surface tension is greater with sodium hydroxide than with ammonia owing to the greater electrolytic dissociation of the former. The surface tension was also lowered by hydrochloric acid but only slightly, M/2 HCl bringing it down to 31.5. This is in accord with Wilson's qualitative conclusions that acids do not increase the surface tension quite as much as pure water. Von Lerch also found a marked effect due to acetic acid; but this acid is miscible in all proportions with benzene and causes benzene and water to become more miscible, so there is nothing surprising about its behavior. The surface tension measurements are confirmed by the electrical ones, for von Lerch found that drops of benzene in caustic soda moved fairly readily under electrical stress, whereas there was almost no movement in presence of sodium chloride or hydrochloric acid. It is possible that other ions might be adsorbed markedly by benzene, but I know of no experiments to show this. Patrick⁶ found that new fuchsine,

¹ Jour. Chem. Soc., **1**, 174 (1849).

² Phil. Mag. (3) **33**, 36 (1848).

³ Jour. Phys. Chem. **19**, 360 (1915).

⁴ Drude's Ann., **9**, 434 (1902).

⁵ HARKINS states that VON LERCH's experiments with dilute caustic soda solution are inaccurate.

⁶ Zeit. phys. Chem., **86**, 545 (1914).

picric acid, salicylic acid, and mercurous sulphate are adsorbed from aqueous solution by mercury, the surface tension of the mercury being lowered as a result of the adsorption. In all four cases the amounts adsorbed varied with the concentration approximately according to a formula of the type found to hold for adsorption from solution by a solid.

The absorption of hydroxyl means practically a concentrating of alkali at the surface of the benzene and consequently a closely adhering film of water. This accounts for Wilson's observation that the drops of chloroform were readily wetted by an alkaline solution. The presence of the surface film of caustic soda solution also accounts for the decreased mobility observed by Wilson.

CHAPTER IV

SURFACE TENSION—BROWNIAN MOVEMENTS

ADSORPTION AND SURFACE TENSION

When a substance dissolves in a liquid, the surface tension between the liquid and the vapor changes, increasing in some cases and decreasing in others. Two solutions of the same density will not necessarily have the same surface tension. For this reason a hydrometer graduated for sulphuric acid solutions will not be accurate for hydrochloric acid solutions, because the amounts of solution which will rise up the stem of the hydrometer will depend on the surface tensions and will therefore not be the same in the two cases. In most cases the surface tensions of solutions will lie between the surface tensions of the constituents; but this is not necessarily true.¹ Röntgen and Schneider² found a maximum surface tension for sulphuric acid and water at about 48 percent H_2SO_4 . Whatmough³ obtained minima for mixtures of acetic acid with benzene, methyl iodide, ethyl iodide, chloroform, or carbon tetrachloride; for carbon bisulphide and ethylene chloride; for benzene and ethyl iodide; for carbon tetrachloride and chloroform, for ethyl acetate and amyl alcohol. Most salts increase the surface tension of the solution, the increase being very nearly proportional to the concentration. The strong bases increase the surface tension but ammonia lowers it and so also do nitric, hydrochloric, and hydrobromic acid. Worley⁴ has discovered an interesting fact. Although sodium chloride increases the surface tension of water, the addition of salt to a solution of aniline in water decreases the surface tension. The sodium chloride decreases the solubility of aniline in water and therefore increases the partial pressure of the aniline vapor.

¹ See FREUNDLICH: *Kapillarchemie*, 58 (1909).

² *Wied. Ann.*, **29**, 165 (1886).

³ *Zeit. phys. Chem.*, **39**, 129 (1902).

⁴ *Jour. Chem. Soc.*, **105**, 260, 273 (1914).

The vapor pressures therefore correspond to a solution richer in aniline than that actually present and the surface tension relations run approximately parallel with the vapor pressures. Worley noticed another curious thing in regard to change of surface tensions of solutions with rising temperature. Since liquid and vapor are identical at the critical temperature, the surface tension becomes zero at the critical point and the surface tension of pure liquids therefore decreases with rising temperature. One might reasonably have expected that the surface tension temperature curves for solutions would run somewhere near parallel to the corresponding curves for the pure constituents; but this is not the case for mixtures of water with aniline or phenol. The surface tensions of the phenol-rich solutions vary relatively little with rising temperature, while the corresponding aniline solutions actually show an increase of surface tension with rising temperature. The explanation seems to be that the ratio of water to aniline or phenol in the vapor increases with rising temperature and that the solutions therefore show surface tensions corresponding to what one might expect of solutions richer in water than they actually are. It is a pity that Worley did not also study some such case as ether and water, where the partially miscible liquid with the lower surface tension has the higher vapor pressure.

The change in surface tension when a solution is formed is also accompanied by a change in concentration, the surface film of the liquid having a different concentration from the mass of the liquid solution. The simple rule in regard to this is that the concentration in the film tends to change so as to decrease the surface tension.¹ Consequently the surface film will be more dilute than the mass of the solution if the dissolved substance increases the surface tension, and will be more concentrated than it, if the solute lowers the surface tension of the solution. An equilibrium will be reached when the change in the surface tension is balanced by the difference of osmotic pressure between the surface film and the mass of the solution. This can be expressed mathematically by the equation²

$$\gamma = - \frac{da}{d\mu}$$

¹ J. WILLARD GIBBS: Scientific Papers, 1, 219.

² Cf. DONNAN and BARKER: Proc. Roy. Soc., 85A, 557 (1911).

where a is the interfacial tension, μ is the chemical potential of the dissolved substance in the aqueous phase, γ is the mass of solute per unit area of interface in excess of that corresponding to the uniform bulk-concentration of the solute in the solution. It will be seen that γ is, in fact, the amount of solute per unit area of interface adsorbed or concentrated in the interfacial transition layer. If we are justified in applying the laws of dilute solutions, the above equation can be written

$$\gamma = - \frac{c}{RT} \frac{da}{dc}$$

where R is the constant of the simple gas equation, T is the absolute thermodynamic temperature and c is the concentration. It is to be noted that these two equations apply only to the case of a substance which is really in solution, a point which is apt to be overlooked in papers on colloids. On the other hand, there are many substances such as soap, saponin, gelatine, which are probably not soluble in water to any appreciable extent; but which form apparent or colloidal solutions with surface tensions lower than those of pure water. In these cases the concentration of the added substance will be higher in the surface film than in the mass of the liquid, but the Gibbs formula will not apply. As a matter of fact with sodium glycocollate, Congo red, methyl orange, and sodium oleate, the adsorptions in the surface are 20–100 times those calculated from the formula.¹

If the difference in concentration between the mass of the solution and the surface layer is set up slowly, one ought to get one value for the surface tension when equilibrium is reached and another if rapid measurements are made on a fresh surface. This has been done by Lord Rayleigh,² though not for a case of true solution.³ The equilibrium or static method consisted in measuring the rise in capillary tubes. The rapid or dynamic method depends on the principle that a jet of liquid issuing under moderate pressure from an elongated, *e.g.*, elliptical, aperture

¹ WILLOWS and HATSCHEK: Surface Tension and Surface Energy, 46 (1915).

² Proc. Roy. Soc., 47, 281 (1890).

³ See however HARKINS and BROWN: Jour. Am. Chem. Soc., 41, 522 (1919).

perforated in a thin plate, assumes a chain-like appearance, the complete period, λ , corresponding to two links of the chain, being the distance traveled over by a given part of the liquid in the time occupied by a complete transverse vibration of the column about its cylindrical configuration of equilibrium. Since the phase of vibration depends upon the time elapsed, it is always the same at the same point in space, and thus the motion is *steady* in the hydrodynamical sense, and the boundary of the jet is a fixed surface. Measurements of λ under a given head, or velocity, determine the time of vibration, and from this, when the density of the liquid and the diameter of the column are known, follows in its turn the value of the capillary tension to which the vibrations are due. By this method the liquid surface may be tested before it is $\frac{1}{1000}$ second old.

Rayleigh's data have been recalculated by Freundlich¹ who added some of his own. These are given in Table XXXVIII.

TABLE XXXVIII.—STATIC AND DYNAMIC SURFACE TENSIONS OF SOLUTIONS

Solution	Concentration	Surface tensions in dynes/cm	
		Static	Dynamic
Water.....		75	75
Sodium oleate . . .	0.025 percent	55	79
Sodium oleate . . .	0.25 percent	26	79
Sodium oleate. . .	1.25 percent	26	62
Sodium oleate..	2.5 percent	26	58
Saponin.....	..	52	73
Heptylic acid . . .	0.005N	54	68

Except in the case of pure water the surface tensions by the static method are lower than those by the dynamic method. One curious point is that the surface tensions by the dynamic method are higher than that of pure water in the case of the two very dilute sodium oleate solutions. Lord Rayleigh did not discuss this point and Freundlich leaves it untouched. In the actual measurements an error of about two percent would account for the difference, which may be due to experimental error. There is another possibility, however, that the sodium oleate is completely

¹ Kapillarchemie, 56 (1909).

hydrolyzed in the dilute solutions and that what is measured by the dynamic method is really the surface tension of a caustic soda solution.

While this set of experiments gives more or less the results that one would expect, it seems impossible to account for the difference between the static and dynamic methods in the case of the adsorption of gases by mercury. Stöckle¹ measured the surface tension of mercury in a vacuum of 0.004–0.001 mm and obtained a value of 436 dynes/cm at 15° regardless whether the measurement was made at once or not. When hydrogen was present, the time factor was important, a value of 470 dynes/cm being obtained when the measurement was made quickly, but dropping to 434 dynes/cm if the mercury were allowed to stand in contact with hydrogen. Similar results were obtained with oxygen, nitrogen, carbon dioxide, and air, Table XXXIX. The general results were confirmed by G. Meyer,² Table XL, who made

TABLE XXXIX.—SURFACE TENSION OF MERCURY

Data in dynes/cm with fresh and old surfaces

Medium	Rapid	After 60'
Vacuum (15°)	436	434
Hydrogen (21°)	470	436
Oxygen (25°).	478	432
Nitrogen (16°)	489	438
Carbon dioxide (19°)	429
Dry air (17°)	476	429
Moist air (17°)	481	

TABLE XL.—SURFACE TENSION OF MERCURY

Data in dynes/cm with fresh and old surfaces

Medium	Vibrating jet	Curvature of surface
Hydrogen...	554	470
Oxygen	504	478
Carbon dioxide	487	480
Nitrogen	496	489

¹ Wied. Ann., 66, 49 (1898).

² Ibid., 66, 523 (1898).

use of Rayleigh's jet method for the rapid measurements and consequently obtained higher values than Stöckle.

It may be easy to see that the adsorption of a gas by mercury should lower the surface tension, but it is not clear why different gases should bring the surface tension down practically to the same value as that found when there is supposed to be no gas present. The dynamic methods should start at the value for mercury in a vacuum if no factor has been overlooked and there is no apparent reason why an unadsorbed gas should raise the surface tension of mercury so much.

Lenard¹ has brought up a point which may have a bearing on this. If we have a partially polymerized liquid such as water, the modification having the lower surface tension will concentrate in the surface. If we form a new surface suddenly, we shall get a higher concentration, temporarily, of the particular modification which has the higher surface tension. If the equilibrium is reached relatively slowly, the dynamic method will give a higher value for the surface tension than the static methods. If equilibrium is reached instantaneously, there will be no difference. We can account for the facts observed with mercury if we make the assumptions that mercury is a partially polymerized liquid, that equilibrium between the modifications is reached practically instantaneously in a vacuum, and that equilibrium is reached relatively slowly in presence of gases. The difficulty with this is that we have no independent proof of these assumptions.

Another hypothetical explanation becomes possible, if we assume that there is not a sharp discontinuity at the surface between liquid and vapor. The Laplace theory of surface tension assumes that there is a perfectly sharp line of demarcation between the two media bounding the surface, for instance,² between liquid and air, while van der Waals postulates a continuous transition.

According to the latter way of looking at things, mercury in a vacuum adsorbs its own vapor forming a thin transition layer varying from the density of liquid mercury at one side to the density of mercury vapor at the other side. If this transition

¹ Cf. AGANIN: *Drude's Ann.*, **45**, 1020 (1914).

² WILLOWS and HATSCHER: *Surface Tension and Surface Energy*, **33** (1915).

film forms instantaneously in a vacuum and relatively slowly in presence of a gas, the surface tension of a fresh surface of mercury in presence of a gas will be higher than the equilibrium surface tension of mercury in a vacuum, and this higher surface tension thus measured will decrease, if the surface is not renewed, down to the equilibrium surface tension of mercury in a vacuum, or below it if the gas is adsorbed markedly at the mercury surface. This explanation seems somewhat more plausible than that of Lenard; but it is open to the same objection that there is as yet no independent proof of the assumptions involved.

Ferguson¹ has shown that the surface tension of benzene is different in air from what it is in carbon dioxide. It is a question of course to what extent this difference is due to the solubilities of the gases in the benzene. Ferguson considers that the nature of the gas is more important than the solubility effect; but he gives no evidence for this. He does, however, mention one interesting and surprising fact that the absolute value of the surface tensions increased slightly as the liquid became more and more saturated, finally reaching a steady value.

From the fact that the lowering of the surface tension is accompanied by an increase in the concentration of the surface film of a true solution, Freundlich² draws the conclusion that this is true in all cases, and that if a dissolved substance lowers the surface tension between the solid and the solution, the dissolved substance is adsorbed; conversely that the dissolved substance is adsorbed only in case it lowers the surface tension at the interface. The conclusion may or may not be right; but the logic is faulty because the two cases are not parallel. The Gibbs relation holds for a true solution, where the difference of concentration is entirely inside the solution phase. Freundlich is extending the relation to a heterogeneous system in which the adsorbed substance is presumably on the outer surface of the solid and by definition cannot diffuse into it because we should then have a solid solution. It is very difficult to prove or disprove Freundlich's conclusion experimentally; but it is a great pity to have people believe, as many now do, that the generalization is based on sound thermodynamics.

¹ Phil. Mag. (6) 28, 403 (1914).

² Zeit. phys. Chem., 57, 424 (1907).

4 The surface tension of solids cannot be measured directly; but Tangl¹ has made some experiments on the surface tension of such pseudo-solids as rubber and paraffin against water.

Solids undoubtedly do have definite surface tensions. In fact, one might consider the melting point as the temperature at which the surface tension overcomes the crystalline forces. In the liquid crystals and the flowing crystals, we have intermediate stages. Reference has already been made to Beilby's experiments on thin gold leaf which became granular when heated.² We shall see later that the phenomenon of sintering depends on surface tension.

BROWNIAN MOVEMENTS

If a stone be dropped into water, it sinks rapidly; but if it be ground into fine particles, the surface is much greater and consequently the particles sink slowly. If the stone were ground into very fine particles, we should expect these to sink very slowly, the rate being a function of the diameter and density of the particles. A formula,

$$V = \frac{2r^2(S - S')g}{9\eta}$$

for this case has been deduced by Stokes,³ where V is the constant rate of fall, r the radius of the particles, S their specific gravity, S' the specific gravity of the liquid, η its viscosity coefficient and g the gravitational constant. Hatschek⁴ has applied this formula to several special cases. For particles⁵ of gold of 1μ radius the rate of fall in water is calculated to be 2.4 mm per minute. With gold particles of $10\mu\mu$ radius the rate of settling in water is about 10 mm per month. For a particle of $10\mu\mu$ radius and a specific gravity of only 3 the calculated rate would be about 1 mm per month. Very small rates of fall have actually been observed.

¹ Drude's *Ann.*, **34**, 311 (1911); cf. JONES: *Zeit. phys. Chem.*, **82**, 448 (1913); RONTGEN: *Wied. Ann.*, **3**, 321 (1878).

² *Proc. Roy. Soc.*, **72**, 226 (1904).

³ *Mathematical and Physical Papers*, **3**, 1 (1901). For modifications and limitations see CUNNINGHAM: *Proc. Roy. Soc.*, **83A**, 357 (1910); *Jour. Am. Chem. Soc.*, **41**, 319 (1919); MILLIKAN: *Phys. Zeit.*, **11**, 1097 (1910).

⁴ *An Introduction to the Physics and Chemistry of Colloids*, 24 (1913).

⁵ Elutriation, or the difference in the rate of settling, is much used in grading powders such as emery, carborundum, ultramarine, kaolin, etc.

Even in air fine particles settle very slowly. A sandstorm in the Grand Canyon may make the air a brick-red color for two or three days.¹ Similar phenomena are to be observed all over the world.²

Ebell³ states that ultramarine will stay suspended in pure water for months when obtained in a very finely divided state by grinding and elutriation. Mülhauser⁴ found that when very finely ground carborundum powder is treated with water, a portion of it does not settle in months and behaves in that respect like colloidal metallic silver. Brewer⁵ points out the slow rate at which clays settle, and raises the question whether extremely finely divided particles settle at all.

If the very finely divided particles do not really settle at all, there must be some factor which neutralizes the action of gravity more or less completely. The experiments of an English botanist, Brown,⁶ give us a clue to the difficulty, though the importance of these experiments was not appreciated until very much later. Brown was studying under the microscope the grains of pollen from *Clarkia pulchella*, and observed that some of them moved about in the liquid. Further experiments showed that practically all finely divided solids kept in continuous motion. Brown considered that he was watching the movements of active molecules.

The zig-zag movements of suspended particles are known as Brownian movements. They are apparently due to the bombardment of the suspended particles by the molecules of the liquid.⁷ On this hypothesis the motion should be more rapid, the smaller the bombarded particles and this proves to be the case. The work of Gouy showed that the hypothesis of molecular agitation gave a satisfactory explanation of the Brownian move-

¹ ELLSWORTH and EMERY KOLB: National Geographical Magazine, 26, 134 (1914).

² See EHRENBURG: Die Bodenkolloide, 209 (1915).

³ Ber. deutsch. chem. Ges., 16, 2429 (1883).

⁴ Zeit. anorg. Chem., 5, 117 (1894).

⁵ Mem. Nat. Acad. Sci., 2, 165 (1884); Am. Jour. Sci. (3) 29, 1 (1885).

⁶ Phil. Mag., 4, 161 (1828); 6, 161 (1829).

⁷ WIENER: Pogg. Ann., 118, 79 (1863); GOUY: Jour. de Phys. (2) 7, 561 (1888); Comptes rendus, 109, 102 (1889); Revue générale des Sciences, 1895, 1.

ments and that all the other tentative explanations were faulty. He showed that the Brownian movements are not due to vibrations transmitted to the liquid under examination, since they persist equally as well, for example, at night in the country as during the day near a populous street where heavy vehicles pass. They are not due to convection currents existing in fluids where thermal equilibrium has not been attained, for they do not change appreciably when plenty of time is given for equilibrium to be reached. Any comparison between Brownian movements and the agitation of dust particles dancing in the sunlight must therefore be set aside. In addition, in the latter case, it is easy to see that the neighboring dust-particles move in general in the same sense, roughly tracing out the form of the common current which bears them along, whereas the most striking feature of the Brownian movements is the absolute independence of the displacement of neighboring particles, so near together that they pass by one another. The movements cannot be due to an effect of light because Gouy was able to vary the intensity of the illumination abruptly a thousand-fold, or to change the color considerably without modifying the phenomena. The nature of the particles does not appear to be of any importance, and it is therefore difficult not to believe that these particles reveal an internal agitation of the fluid, the better the smaller they are, much as a cork follows better than a large ship the movements of the waves of the sea.

The distance between the two end-points as a particle zig-zags forward and back is usually defined as twice the amplitude. Svedberg¹ found that for different solutions the product of the amplitude, A , into the viscosity, η , is a constant and that the amplitude divided by the time which the particles take in passing through that distance is also a constant. These results are in qualitative agreement with a theoretical formula deduced by Einstein.² If one knows the amplitude and the time, one can calculate the speed of the particles. For platinum particles with a diameter of 10–50 $\mu\mu$, Svedberg found speeds of 200–400 $\mu\mu$ per second. Perrin³ considers that errors of measurements vi-

¹ *Zeit. Elektrochemie*, **12**, 835, 909 (1906).

² *Drude's Ann.*, **17**, 549 (1905); **18**, 289, 371 (1906).

³ *Brownian Movement and Molecular Reality*, 22 (1910).

tiate these data. He says that the speed of a granule in suspension cannot be measured accurately.

Even though quantitative measurements may be inaccurate, it is desirable to have a general idea of the magnitude of the phenomenon. From Exner's¹ experiments it appears that particles with a diameter larger than 4μ show no perceptible Brownian movements. Particles smaller than 0.1μ begin to show lively movements,² while particles with diameters of about 10μ give apparent trajectories up to 20μ .

Perrin³ came to the conclusion that the gas laws must apply to dilute emulsions. "Let us suppose that it is possible to obtain an emulsion, with the granules all identical, an emulsion which I shall call for shortness, uniform. It appeared to me, at first intuitively, that the granules of such an emulsion should distribute themselves as a function of the height in the same manner as the molecules of a gas under the influence of gravity. Just as the air is more dense at sea-level than on a mountain-top, so the granules of an emulsion, whatever may be their initial distribution, will attain a permanent state where the concentration will go on diminishing as a function of the height from the lower layers; and the law of rarefaction will be the same as for air."

To test this hypothesis Perrin prepared a uniform suspension of purified gamboge in water by means of fractional centrifuging. The results confirmed the hypothesis. With gamboge particles 0.3μ in diameter a rise of 30μ was sufficient to lower the concentration to a half of its value, 30μ in the gamboge suspension being equivalent to 6 kilometers in the air.⁴ Satisfactory results have also been obtained by Zangger⁵ for drops of mercury, by Brillouin⁶ for gamboge in glycerol solutions having a viscosity 160 times that of water, and by Iljin.⁷ This cannot be true over any appreciable range because it would mean that the concentration would drop to one-billionth in a rise of about a millimeter, which would mean that no colloidal solution would appear uni-

¹ Sitzungsber. Akad. Wiss. Wien., **56** II, 116 (1867).

² ZSIGMONDY: Kolloidchemie, 18 (1912).

³ Brownian Movement and Molecular Reality, 22 (1910).

⁴ PERRIN: Brownian Movement and Molecular Reality, 43 (1910).

⁵ Zeit. Kolloidchemie, **7**, 216 (1911).

⁶ Ann. Chim. Phys. (8) **27**, 412 (1912).

⁷ Zeit. phys. Chem., **83**, 592 (1913).

form. It has been suggested by Burton that the concentration increases with increasing depth only up to about a certain value and then remains practically constant.

Einstein¹ assumes that suspended particles will behave exactly like dissolved particles, exerting an osmotic pressure and diffusing through the solvent.² Instead of the van't Hoff expression that the osmotic pressure, P , of a dissolved substance is given by the equation

$$PV = nRT$$

Einstein deduces the equation

$$PV = \frac{n}{N} RT,$$

where n is now the number of suspended particles and N is Avogadro's constant or the actual number of molecules in a gram-molecule. Following this up he deduces for the rate of diffusion the equation

$$D_x = \sqrt{\frac{RT}{N\pi} \frac{t}{3r\eta}}$$

where D_x is the displacement in a given direction, t is the time, R is the gas constant, T the absolute temperature, N is the Avogadro constant, r is the radius of the particles and η is the viscosity of the liquid. This has been confirmed quantitatively by Perrin who gets a mean value³ of about 68×10^{23} for N . In regard to this he says:⁴ "Thus the molecular theory of the Brownian movement can be regarded as established experimentally, and it becomes very difficult to deny the objective reality of molecules. At the same time we see the law of gases, already applied by van't Hoff to dilute solutions, extended to uniform emulsions. The Brownian movement offers us, on a different scale, the faithful picture of the movements possessed,

¹ Drude's Ann., 17, 549 (1905); 19, 280, 371 (1906). See also SMOLUCHOWSKI: Ibid., 21, 756 (1906).

² It must be remembered that Einstein has ignored all adsorption of the liquid by the suspended particles. He did the same thing when deducing a formula for the viscosity of colloidal solutions and came to the erroneous conclusion that the viscosity depends only on the volume and not on the size of the suspended particles.

³ PERRIN: *Die Atome*, 123 (1914).

⁴ PERRIN: *Brownian Movement and Molecular Reality*, 46 (1909).

for example, by the molecules of oxygen dissolved in the water of a lake, which, encountering one another only rarely, change their direction and speed by virtue of their impacts with the molecules of the solvent.

"It may be interesting to observe that the largest of the granules, for which I have found the laws of perfect gases followed, are already visible in sunlight under a strong lens. They behave as the molecules of a perfect gas, of which the gram-molecule would weigh 200,000 tons.

"I add lastly that all the measurements detailed in this paragraph have been made on dilute emulsions, which in the parts richest in granules only contain a thousandth part of resin, and where the osmotic pressure does not reach a thousand millionth of an atmosphere."

If we substitute four times the amplitude for D_x ($D_x = 4A$) in Einstein's formula, t will be the time required for the particle to make one complete oscillation.¹ Einstein's formula therefore becomes

$$(4A)^2 = \frac{\pi RT}{N} \frac{t}{3r\eta}$$

If we are considering particles of the same size in various liquids we may write the equation $A^2 = k.t/\eta$ if we are working at constant temperature. "Since, by the kinetic theory, the average kinetic energy of a particle is the same as the average kinetic energy of a molecule, and the molecules of all fluids at the same temperature have the same average kinetic energy, we should expect the average velocity of all the particles to be the same, provided their masses are the same, whatever the liquid in which they are moving." Einstein's formula therefore leads to the set of relations: $A\eta = \text{const.}$; $D_x = \sqrt{T/\eta}$ and $D_x/\sqrt{t} = \text{const.}$

As has been pointed out, Svedberg had discovered independently that the product of the amplitude into the viscosity was a constant at constant temperature. Exner² found that the ratio of displacements at 20° and 71° is 1:1.6 while the ratio of the corresponding values of $\sqrt{T/\eta}$ for water at these two tempera-

¹ BURTON: The Physical Properties of Colloidal Solutions, 76 (1916).

² BURTON: The Physical Properties of Colloidal Solutions, 77 (1916).

tures is 1:1.7. Seddig¹ has shown by means of a photographic method in conjunction with the microscope, that finely divided cinnabar in water obeys Einstein's formula, the greatest departure from the theoretical value being 6 percent.

Chaudesaigues,² working with an emulsion of gamboge, varied the viscosity of a solution by adding sugar. In this way he carried out observations on two solutions containing the same-sized particles at the same temperature, the viscosities of which were in the ratio 1:4 and found that the motion was twice as fast in the less viscous solution as it was in the solution of higher viscosity. Chaudesaigues observed the velocities of particles of gamboge with radii respectively 4.5×10^{-5} cm and 2.3×10^{-5} , practically a ratio of 2:1, and found that these velocities varied inversely as the square of the radii. He also observed the distances described by 50 grains, each of radius 2.13×10^{-5} cm during successive intervals of 30 seconds each and obtained the following results: on the average the particles moved

6.7, 9.3, 11.8 and 13.95 microns in

30, 60, 90 and 120 seconds. The square roots of the times are proportional to the numbers,

6.7, 9.46, 11.6 and 13.4, giving an ideal confirmation of this point.

It was first pointed out³ by Smoluchowski⁴ that we should expect to have the Brownian movements in gases as well as in liquids and he quotes from Bodaszewski⁵ and O. Lehmann⁶ as to the dancing movements executed by the particles of fumes of ammonium chloride, acids, phosphorus, etc. which they compared to the Brownian movements in liquids and interpreted as molecular movements.⁷ The formulas of Einstein and Smoluchowski are based on the Stokes law, which does not hold for gases under low pressure where the mean free path of the gas molecules

¹ Phys. Zeit., **9**, 465 (1908).

² Comptes rendus, **147**, 1044 (1908).

³ BURTON: The Physical Properties of Colloidal Solutions, 85 (1916).

⁴ Drude's Ann., **21**, 756 (1906).

⁵ Kosmos, **7**, 177 (1882); Beibl., **8**, 488 (1883).

⁶ Molekularphysik, II, 5.

⁷ "The sun," says Daniel Culverwell, "discovers atoms, though they be invisible by candle light, and makes them dance naked in his beams."

is large relatively to the radius of the particles. Ehrenhaft¹ was the first to carry out direct measurements on the Brownian movement of particles in gases. He found that, as theory predicts, there is a much livelier motion in gases than in liquids; at the same time the action of gravity in causing vertical descent of the particles is also much more apparent in gases than it is in liquids. For comparatively large particles in the smoke of cigars and cigarettes and in the fumes of ammonium chloride, he observed an undoubtedly zigzag Brownian movement, while with smaller particles obtained by a spark discharge between zinc, platinum, or silver electrodes, Ehrenhaft concluded that he has proved without a doubt the existence of a motion in gases completely analogous to the Brownian movement in liquids.

It is more difficult to recognize this motion in gases on account of disturbing convection currents and the action of gravity. For the heavier particles, the velocity due to the force of gravity completely overshadows that due to the molecular shocks, while the opposite is the case with the very small particles. In Table XLI are given the velocities impressed by molecular shocks and by the force of gravitation, respectively, on silver particles of

TABLE XLI.—BROWNIAN MOVEMENTS IN GASES

Radius of silver particles	Velocity due to molecular shocks	Velocity due to gravity
1 μ	63 0 μ /sec.	1.2 μ /sec.
5 μ	28 0 μ /sec.	30.0 μ /sec.
10 μ	20.0 μ /sec.	120.0 μ /sec.
50 μ	8.9 μ /sec.	3.0 μ /sec.
100 μ	6 3 μ /sec.	12 0 μ /sec.
500 μ	2 8 μ /sec.	300.0 μ /sec.
1 μ	2 0 μ /sec	1200 0 μ /sec.

various sizes (density 10.5). These numbers show that when we reach particles having diameters of the order of the wave-length of light the two velocities do not differ materially. As we deal with smaller particles, the velocity induced by gravity soon becomes negligible, while with particles increasing above 0.1 μ , the motion due to gravity soon dominates the situation. This is

¹ Sitzungsber. Akad. Wiss. Wien., 116 IIa, 1139 (1907).

in keeping with what Ehrenhaft found. Particles, the linear dimensions of which were of the order of the size of the mean free path of gas molecules (0.1μ), and somewhat larger particles, fall in a zig-zag line, the velocity due to gravitation being greater than that due to molecular shocks. Particles, which are near the limit of visibility in the ultra-microscope ($1\mu\mu$), are in such lively molecular motion that the vertical gravitational velocity is completely masked. Ehrenhaft viewed silver particles that remained in lively motion in the air of his ultra-microscope cell for some thirty minutes. His measurements on the cigarette smoke particles gave a mean velocity of $25\mu/\text{sec.}$ and on the smaller particles of silver, $46\mu/\text{sec.}$

Much interesting work has been done in this field by De Broglie.¹ Both Ehrenhaft and De Broglie have found that these silver particles suspended in air, are charged and, by measuring the velocity impressed on them by a known electric field, have come to the conclusion that the charge is that of one electron. The values that they find for this charge,² e , are respectively 4.6×10^{-10} and 4.5×10^{-10} electrostatic units. Wells and Gerke³ have measured the velocity of smoke particles in an electrical field and have determined the size of the particles from the resulting data.

It seems to be accepted pretty generally that the work of Perrin, Svedberg, and others has established the practical continuity between suspended particles and dissolved substances; but this seems to be an overhasty conclusion. The molecular weight of a dispersed substance, as calculated from any of Einstein's formulas means something entirely different, if it means anything at all. We can determine the molecular weight of liquid benzene approximately from a measurement of the surface tension; but it is absurd to say that suspending fine drops of benzene in water causes the molecular weight of benzene to be equal to 200,000 tons.⁴ We are talking about entirely different things in the two cases. What we mean is that dissolved ben-

¹ Comptes rendus, **146**, 624, 1010 (1908); **148**, 1163, 1315 (1909).

² See also MILLIKAN: Phil. Mag. (6) **19**, 209 (1910).

³ Jour. Am. Chem. Soc., **41**, 312 (1919).

⁴ Such a hypothetical gas would have a density roughly a million times that of metallic copper.

zene has a molecular weight of 78, and that liquid benzene suspended in water behaves or may behave as if it were a dissolved substance having a molecular weight of 200,000 tons, more or less. As a matter of fact the experiments bring out clearly the enormous difference between a solution and a suspension.

The safe ground to take is: that the Brownian movements are due to the incessant movements of the molecules of the fluid; that the Brownian movements tend to make finely-divided, suspended particles distribute themselves uniformly throughout the liquid; that the uniform distribution is affected by the force of gravity as in the case of a gas; and that the Brownian movements, though causing diffusion, give rise to no appreciable osmotic pressure.

Very finely divided particles (less than 0.5μ for instance) will be kept in suspension indefinitely by the Brownian movements, so long as the particles remain finely divided. If, however, two or more particles agglomerate or coalesce, the force of gravity may cause the particles to settle to the bottom of the containing vessel.

CHAPTER V

COALESCENCE

COALESCENCE OF LIQUIDS

If two small drops of a pure liquid are brought in contact, they run together and form a larger drop. The two small drops are therefore instable with respect to a larger drop. Consequently we should expect the small drop to distill over to, and condense on, a larger drop. This is equivalent to saying that the greater the curvature of the drop, the higher the vapor-pressure. This conclusion was drawn by Lord Kelvin, then William Thomson,¹ many years ago. He reached his conclusion in a slightly different way. If we have a capillary tube dipping into a liquid, the whole being in a closed vessel containing only the liquid and its vapor, the raised liquid surface in the capillary must be in equilibrium with the main surface of the liquid if the system is all at the same temperature. The pressure of the vapor varies, however, at different levels in consequence of gravity. Consequently the concave surface of the liquid meniscus must have a lower vapor-pressure than the plane surface of the liquid. The converse must also be true that the convex surface of a drop must have a higher vapor-pressure than the plane surface of the liquid. This difference will be greater the greater the curvature of the surface or, in other words, the smaller the drop. The actual difference in vapor pressure between the highly curved surface in a capillary tube and the nearly plane surface in a wide vessel is very small. It amounts to one-thousandth of the vapor-pressure in a capillary tube in which water would rise thirteen meters.

Lord Kelvin² considered that this theory, originally due to Laplace, is applicable to cases in which the radius of curvature is

¹ Phil. Mag. (4) **42**, 448 (1871).

² Ibid. (4) **42**, 451 (1871).

as small as 1.2μ ; but he thinks that we are not entitled to push it much further. Consequently he believes that the formulas he has deduced are not applicable to the vapor pressures of moisture retained by such substances as cotton cloth and oatmeal at temperatures far above the dewpoint of the surrounding atmosphere. He believes, however, that the difference is quantitative and not qualitative; that the adsorption of vapor by fibrous and cellular organic structures is a property of matter continuous with the adsorption of vapor into a capillary tube.

The converse of the theory is also true that liquid will distill into a capillary tube closed at the lower end until the height of the meniscus above the level of the liquid is the same as the height to which the liquid would have risen in the capillary tube if the lower end had been open. Bacon¹ has done the experiment successfully with ether, though the rate of distillation is very low.

The rate at which small drops coalesce depends on the mobility of the liquid. With viscous liquids such as cooling lavas or slags, we know that we get all sorts of phenomena which do not correspond to equilibrium relations, and it is probable that jellies are rarely in true equilibrium.

COALESCENCE OF SOLIDS

While it is perfectly familiar to all of us that two small drops of a pure liquid will coalesce readily to form a larger drop, all our ordinary experience is the other way in regard to solids and yet, theoretically, finely divided solids behave like finely divided liquids in many respects. A very finely divided powder must have a higher vapor-pressure, a lower melting-point, and a greater solubility² than the same substance in a more coarsely crystalline form. When yellow phosphorus is placed in a tube, the air removed, and the tube then sealed, it is said by Herman² and by J. Lawrence Smith³ that crystals form in a short time on the walls of the tube and may grow to a diameter of 3–5 mm in the course of a month or six weeks. Crystals of iodine having a diameter of 2–3 mm were kept in the dark for eight years,

¹ Phys. Rev., **20**, 1 (1905).

² OSTWALD: Zeit. phys. Chem, **35**, 495 (1900).

³ Jour. Chem., Soc., **27**, 869 (1874).

the temperature varying from 0° to 24° . At the end of that time von Jonstorff¹ found that the smaller crystals had mostly disappeared and that the crystals were now about 4–5 mm in diameter. Hautefeuille and Perrey² found that at a dull red heat hydrochloric acid gas at a pressure of three atmospheres causes amorphous alumina to change into corundum, titania into anatase and zirconia into a crystalline form. The crystallization of the alumina is believed to be due to the successive formations and decompositions of an aluminum chloride. Emden³ has shown that ice grains as large as hazel nuts may be grown from snow slush with original small ice nuclei, kept in sealed vessels for several weeks at a constant temperature of 0° .

Pawlow⁴ states that crystals of salol which were 2μ in diameter melted 1.1° lower than crystals 40μ in diameter. Comparing a fine dust of less than 2μ diameter with crystals 0.5–2.0 mm diameter, differences of 4° – 7° were obtained with salol, antipyrin, and phenacetin; but it seems probable that part of these differences is due to impurities and part to experimental error.

Hulett⁵ found practically no difference for the solubility of calcium sulphate in water until the radius of the crystals was less than 2μ . Changing from 2μ to 0.3μ caused an increase in solubility of nearly 20 percent. A coarsely crystalline barium sulphate (1.8μ) was soluble 2.29 mg per liter at 25° . When ground in an agate mortar to 0.1μ the solubility rose to 4.5 mg per liter. The corresponding figures with natural barytes were 2.38 mg and 6.18 mg. Red mercuric oxide has a solubility of 50 mg per liter at 25° ; when ground to a fine powder the color becomes yellow and the solubility increases to 150 mg per liter. Jones and Partington⁶ made conductivity measurements on saturated gypsum solutions. They found no variation with size of crystals when the radius exceeded 50μ .

This parallelism between small grains and small drops makes one wonder whether the apparent failure of solid particles to

¹ Ber. deutsch. chem. Ges., 10, 866 (1877).

² Comptes rendus, 110, 1028 (1890).

³ VON ENGELN: Am. Jour. Sci. (4) 40, 461 (1915).

⁴ Zeit. phys. Chem., 65, 1 (1908); 68, 366 (1909).

⁵ Ibid., 37, 385 (1901).

⁶ Jour. Chem. Soc., 107 II, 1019 (1915).

coalesce may not be due to experimental error. If we precipitate copper electrolytically on copper, we get a mass which does not differ materially in properties from cast copper having the same size of crystals.¹ The successive layers of copper coalesce to a uniform mass. On the other hand if we electroplate nickel on nickel without taking special precautions, we get a film of nickel which does not adhere. The reason for this is that the original nickel had an oxide film over the surface and the electrolytically precipitated nickel never really came in contact with the nickel electrode. If the oxide film is removed, the plating of nickel on nickel² is as simple as the plating of copper on copper. A silver halide adheres well to a silver anode if the conditions are such that the halide is formed in actual contact with the metal.³

If a plate were broken without chipping, the two pieces would fit together perfectly and should cohere, showing no signs of a break. This does not happen because of the film of condensed air which acts as an elastic cushion and keeps the two parts from actually being brought in contact.⁴ A corollary from this is that if one were to break a plate in an absolute vacuum and were to bring the pieces together in the same vacuum, the plate should theoretically be as good as new. This is not likely to happen practically, because we cannot get an absolute vacuum. If we heat the fragments of any broken object, several things happen. At the higher temperature less gas is adsorbed and it is held less firmly. The solid is likely to become more malleable and it is therefore easier to make contact at a number of points. All chemists know that it is easy to make two glass rods unite at temperatures at which the glass is still very viscous. It may be urged that glass, at those temperatures, is unquestionably a liquid and not a solid. This criticism does not apply to platinum. To weld platinum it is only necessary to put two clean pieces of platinum in contact, to heat them to a moderate temperature far below the melting-point of platinum, and to give them a light tap with a hammer. Since the object in these cases

¹ BENNETT: Jour. Phys. Chem., **16**, 294 (1912).

² SNOWDON: Jour. Phys. Chem., **10**, 134 (1906).

³ REEDY: Am. Jour. Sci. (4) **40**, 407 (1915).

⁴ See BREUER: *Kitte and Klebstoffe*, 23 (1907).

is to bring two like surfaces into intimate contact, it is easy to see why clean surfaces are essential when soldering or brazing metals, and why it is important to use a flux. When iron is treated with sodium amalgam as a preliminary to dry-gilding,¹ part of the effect of the sodium amalgam is to clean the surface of the iron. Cold sodium cuts readily while warm sodium sticks to the knife.²

In some cases two surfaces will unite fairly readily. This is very noticeable with unvulcanized rubber from which it should follow that vulcanized rubber adsorbs air much more strongly. I do not know of any experiments along this line. Willows and Hatschek³ point out that copper can be polished to such a degree that a cube of this metal will support eleven others merely placed in contact. This means that 1 cm² of surface carries a mass of copper 11 cm long and 1 cm square, a weight of about 98 grams. Polished plane surfaces of glass are apt to stick together. Usually this is to be avoided; but Parker and Dalladay⁴ have taken advantage of this property. Glass surfaces can be polished without difficulty so as to be so nearly plane or so nearly of the same curvature that they show less than one interference fringe per inch when placed together and examined by light reflected from the interfaces. These surfaces may be brought into optical contact so that the two pieces of glass act optically as if they were one block by applying a pressure of several pounds per square inch. The two pieces can, however, be separated easily by sudden heating or cooling, by a shearing force, or by the application of liquids which creep in between the surfaces. By selection of the proper temperatures and pressures it has been found possible to weld two such pieces. It was found essential that the temperature at which union took place should not only be far below the melting-point of the glasses to be joined, but also below the annealing temperature, for even at that temperature a very slight strain would cause deformation of worked glass surfaces. At 60° below the annealing temperature it was found that two pieces of glass in optical contact would unite within an

¹ KIRCHMAN: Jour. Chem. Soc., **26**, 418 (1873).

² McDONALD: Chem. News, **97**, 73 (1908).

³ Surface Tension and Surface Energy, 8 (1915).

⁴ Engineering, **103**, 23; Jour. Franklin Inst., **183**, 369 (1917).

hour and that any slight deformation produced by the compression could be remedied by a few strokes of the polishing tool.

Mr. Jerome Alexander has called my attention to the fact that freshly split pieces of mica can be made to coalesce by pressing them between the fingers. After they have been exposed to the air for five or ten minutes, it is impossible to make them unite in this way. This is undoubtedly due to the formation of a surface film, because Lord Rayleigh¹ found that freshly split surfaces of mica attract to themselves at once a coating of moisture which is replaced or supplemented in a few hours by a layer of grease. The fresh surface conducts electricity, while an old surface, in which the moisture has presumably been replaced by grease, insulates well. I have been told that some of the electrical companies make mica blocks by compressing scrap mica; but I do not know any of the details of the process. Horn waste and tortoise-shell waste may be worked up into solid masses by high pressure and moderate heat.²

While it is not possible as a usual thing to mend a broken object by pressing the two pieces together at ordinary temperatures, Spring³ has shown that powders may be welded into massive blocks by the use of sufficiently high pressures. This means that the pressure has been sufficient to squeeze out the air films coating the powders.

Since solids will coalesce when heated and subjected to pressure, there is no reason why some solid powders should not coalesce to some extent under the influence of gravity when heated. This is known as sintering or sometimes as fritting. The two terms are not distinguished as sharply as they might be.⁴ Sintering should be used when a powder coalesces without melting or with but slight fusion, so that the product is still granular and more or less porous. Fritting should be used when the fusion is quite marked and the product is distinctly glassy. The forma-

¹ Scientific Papers, **3**, 523 (1902).

² KOLLER: The Utilization of Waste Products, 62 (1915).

³ Bull. Acad. roy. belg. (2) **49**, 323 (1880); Ann. Chim. Phys. (5) **22**, 170 (1881); Ber. deutsch. chem. Ges. **15**, 395 (1882); Bull. Soc. chim., Paris, (2) **40**, 520 (1883); FRIEDEL: Ibid. (2) **39**, 626; **40**, 526 (1883); JANNETZ, Neel and Clermont: Ibid. (2) **40**, 51 (1883); Tamman: Zeit. Elektrochemie, **15**, 447 (1909).

⁴ Percy's Metallurgy: Fuel, 46, 280 (1875).

tion of bricks and pottery involves sintering; the materials for glazes are fritted. There has been some question whether sintering could take place without at least incipient fusion. Lucas¹ maintained that it was a property of amorphous substances only, in which case it would be nothing more than the slow and partial coalescence of very viscous drops. Day and Allen² found that powdered glasses sinter slowly or rapidly several hundred degrees below the melting temperature of crystals of the same composition. The first traces of sintering appear earlier the finer the powder and the slower the heating. There is no doubt that the sintering of powdered glasses is due to flow in a supercooled liquid and that it is a phenomenon of viscosity and surface tension. Powdered crystalline feldspars do not sinter readily below their melting temperature and, at first, Day and Allen were inclined to suspect that pure, dry, stable crystals would not sinter at all. Their final experiments, however, showed that the purest crystalline feldspar which they could prepare still sintered, though very slowly. Kohlschütter³ found that porous silver obtained by reducing silver salts in different ways, sintered at temperatures from 200°. Instead of concluding that a crystalline substance can sinter, he drew the surprising conclusion that Lucas was right and that therefore the degree of sintering of the silver was a measure of the amount of amorphous silver present, even though he points out the relation between the porosity and the sintering.

Other things being equal the contraction or sintering is greater the higher the temperature, and consequently the higher the temperature the denser the solid. Bricks are less porous the higher the temperature of burning. Of course if the temperature is reached at which vitrification takes place a new phenomenon occurs. Magnesia is more dense the higher it is heated⁴ and so is lime.⁵ While it is unquestionably true that sintering will take place less readily with a pure crystalline substance than with an amorphous one or with one containing impurities which

¹ Zeit. phys. Chem., **52**, 327 (1905).

² Carnegie Inst. Pub., **31**, 59 (1905); Zeit. phys. Chem., **54**, 39 (1906).

³ Liebig's Ann., **398**, 37 (1913); REEDY: Am. Jour. Sci. (4) **40**, 407 (1915).

⁴ DITTE: Comptes rendus, **73**, 270 (1861); MOISSAN: Ibid, **118**, 506 (1894).

⁵ WRIGHT: Zeit. anorg. Chem., **68**, 397 (1910).

lower the melting-point¹ and cause a portion of the mass to soften long before the whole mass is fused, this does not prevent sintering occurring with perfectly pure crystalline substances. The technical advantage of impurities is shown in the case of magnesia.² The crystalline Styrian magnesite is less pure than the amorphous Grecian magnesite, containing more iron. It therefore sinters more readily and at a lower temperature. It is often preferred for this reason to the purer Grecian magnesite, which must either be burned at a higher temperature or must have some bonding material added which will cause sintering at lower temperatures. Of course, the material which sinters at a low temperature will not stand up at so high a temperature as a purer substance which has been shrunk in an electric furnace at a higher temperature.

The sintering of tungsten³ and of tantalum⁴ powder is a technical process carried on far below the melting-point of tungsten, and not depending, so far as we know, on the presence of impurities, though these may be present. Another interesting case of sintering occurs in the gold assay.⁵ After parting, the cornets are of a dull brown color and very friable. When annealed at a bright-red heat they sinter very much and become a pure gold-yellow color. This has been studied in detail by Hanriot⁶ who took an alloy containing four parts of silver to one of gold and dissolved the silver with nitric acid. The gold was left in a spongy brown form which decreased rapidly in bulk on heating and became gold color. Wöhler⁷ has shown that the glowing of heated chromic oxide jellies is the result of rapid sintering and not of the formation of an allotropic modification.

Soot becomes sandy if heated too long or too hot. The density of red phosphorus depends on the heat treatment. Many precipitates sinter or agglomerate on standing, though the change is not usually called that. The agglomeration is often accompanied

¹ ENDELL: *Silikat-Zeitschrift*, **2**, 1, 25 (1914).

² HAVARD: *Refractories and Furnaces*, 89 (1912).

³ RUFF: *Zeit. angew. Chem.*, **25**, 1889 (1912).

⁴ SIEMENS and HALSKE: *Jour. Soc. Chem. Ind.*, **23**, 206 (1906).

⁵ Percy's *Metallurgy: Silver and Gold*, 268 (1880).

⁶ *Comptes rendus*, **151**, 1355 (1910); **152**, 215 (1911); cf. PRAT: *Ibid.*, **70**, 841 (1870).

⁷ *Zeit. Kolloidchemie*, **11**, 241 (1912).

by increased resistance to chemical action. Strongly heated lime reacts very slowly with carbon dioxide.¹ After short ignition, silica dissolves in a boiling solution of potassium or sodium carbonate, but does not if ignited for a long time. Freshly precipitated arsenic sulphide gives off much hydrogen sulphide when boiled with water; but does not after being heated² at 125°. Pulverulent iron burns in the air while massive iron does not. The action of alkali on hydroxides, and of gelatine and ammonia or potassium bromide on silver bromide is decreased enormously if the precipitates are allowed to stand over night. Holmes and Fall³ have made a quantitative study of the change in peptizability of ferric arsenate, so-called, with time of standing.

A plastic substance is one which can be moulded by pressure.⁴ This connotes that any break due to the deformation is self-healing. A mobile liquid is not plastic, because it will not retain its shape. With increasing viscosity a liquid becomes plastic. Molasses candy is plastic until it crystallizes. Semifused glass is plastic. The time factor may be important. Sealing-wax is brittle if the pressure is applied rapidly; but is plastic if the rate of deformation is low. Since metals and other solids coalesce under high pressure, there is no reason why they should not be plastic under the same conditions, as indeed they are. We make use of this property when squirting metals into rods or pipes. Under high pressure ice is also plastic. It has been claimed by Spring⁵ and by Kahlbaum⁶ that solids become almost like mobile fluids under high pressure; but it seems to have been proved conclusively by Spezia⁷ that this not true when the pressure is uniform and that the apparent fluidity occurs only when there is a shearing force. The question of unequal pressure has been

¹ RAOULT: *Comptes rendus*, **92**, 189 (1881); SOSMAN, HOSTETTER and MERWIN: *Jour. Washington Acad. Sci.*, **5**, 563 (1915).

² RAMMELSBERG: *Jour. Chem. Soc.*, **26**, 242 (1873); cf. LAUFER: *Ber. deutsch. chem. Ges.*, **11**, 60, 935 (1878).

³ *Jour. Am. Chem. Soc.*, **41**, 713 (1919).

⁴ DUFF: *A Text-Book of Physics*, 4th Ed., 119 (1916).

⁵ *Bull. Acad. Soc. belg.* (2) **49**, 364 (1880).

⁶ *Verh. Naturforscherges. Basel*, **15**, 14 (1903).

⁷ *Atti. Accad. Sci. Torino*, **45**, 525 (1911); **46**, 682 (1912).

discussed in some detail by Johnston.¹ Iron filings in presence of a magnet might be considered a special case of plasticity, though not one of any great interest. Another special case of partial plasticity is the mineral itacolumite² which is said to have something akin to a series of ball-and-socket joints. Each ball and socket does not admit of a great play, and is not smooth and perfect like that of the joint of a limb. The stone is built up of grains and masses of grains, which are loosely coherent and form irregular cavities in which are engaged projecting parts of other grains or masses of grains of sand, susceptible of a slight motion in the cavity, in some cases in one direction, and in others in several or in all directions. This freedom of motion is of the true quality of a ball-and-socket joint. Perhaps it would be better to call this mineral flexible rather than plastic.

Between the extreme cases of a solid such as a metal and a liquid such as glass or molasses candy, we have the intermediate case of putty which is whiting and oil, or a solid with a liquid film around it. If a liquid is adsorbed strongly by a solid, thin films of the liquid will hold the solid particles together, while still permitting them to move relatively to one another. The tendency of liquid surfaces to coalesce causes any break to heal. A liquid film may therefore act as a bond for solids and may make the mass plastic. Oil is used as a binder in roads and to make putty out of calcium carbonate. Everybody knows that dry sand cannot be moulded whereas wet sand can. Fondant consists of very small crystals of sugar made plastic by a syrupy film of invert sugar and water. Plastic dynamite is made by adding three parts of nitroglycerine³ to one part of diatomaceous earth. Bingham⁴ has made a preliminary study of the concentration at which plasticity begins or ends. If a finely powdered solid is added to a liquid, the viscosity of the liquid is increased or the fluidity, which is the reciprocal of the viscosity, is decreased. The fluidity was calculated from the rate of flow of the liquid through a viscosimeter. At temperatures between 25° and 60°

¹ Jour. Am. Chem. Soc., **34**, 788 (1912); JOHNSTON and ADAMS: *Am. Jour. Sci.* (4) **40**, 351 (1915).

² WETHERILL: *Chem. News*, **22**, 266 (1870).

³ THORP: *Outlines of Industrial Chemistry*, 3d Ed., 482 (1916).

⁴ *Am. Chem. Jour.*, **46**, 278 (1911); *Jour. Franklin Inst.*, **181**, 845 (1916).

the fluidity dropped to zero at the same concentration, so the concentration for zero fluidity is independent of the temperature over the range studied. With infusorial earth in water, zero fluidity was reached at a volume concentration of about 13 percent solids; with China clay at about 4 percent; with the graphite used in Acheson's aquadag zero fluidity was reached at a volume concentration of about 5.5 percent graphite; and with an unspecified clay at about 19.5 percent clay. With infusorial earth in alcohol, zero fluidity was reached at a volume concentration of about 12 percent solids. The mixtures having zero fluidity are not stiff and will not maintain their shape. At higher concentrations there is a change from viscous flow to plastic flow. The distinction made by Bingham is that with viscous flow any shearing force—no matter how small—will produce permanent deformation, whereas, in the case of plastic flow, it is necessary to use a shearing force of finite magnitude in order to produce a permanent deformation. It seems reasonable to assume that we reach zero fluidity when liquid enough is added to the solid to begin to scatter the particles, in other words, when about enough liquid is added to fill the voids. This is true in one case studied by Bingham. The clay referred to contained 81.6 percent voids and required 80.5 volume percent of water to bring it to zero fluidity. The two values would only be identical in case the volume of the adsorbed water just equalled the volume of the adsorbed air. Of course this very important generalization of Bingham's must be tested in more cases before it can be considered as definitely established; but it is so obvious, after it has been pointed out, that it must be approximately true. This discovery of Bingham's may be of distinct importance in the paint industry. The oil requirement for a given pigment is a very arbitrary amount and experts often differ widely in their values. Reproducible figures could be obtained if in each case there was determined the amount of oil necessary to give zero fluidity. Since this is more oil than painters wish to use, it might be advisable to adopt as the standard, some definite fraction of the amount of oil necessary to produce zero fluidity.

Emley¹ has made some determinations on the viscosity of lime pastes. Judging from the diagram given, the viscosity

¹Trans. Am. Ceramic Soc. 15, 401 (1919).

would become infinite or the fluidity zero when there was about 50 percent of hydrated lime in the paste. Since Emley used the Clark viscosimeter, one does not know to what extent his results are comparable with those of Bingham.

Since the concentration producing zero fluidity apparently depends on the volume of the voids, it is necessary to consider approximately what this may be. If equal spheres are taken and are piled so that each sphere is directly on top of another—minimum or cubical piling—the voids constitute theoretically about 48 percent of the whole, irrespective of the size of the spheres. If the spheres are piled so that each one rests equally on the four in the layer below—maximum or hexagonal piling—the theoretical percentage of voids is nearly 26, again irrespective of the size of the spheres. With solids of different sizes and different shapes, the voids may theoretically be made almost anything. If the solids have condensed air films round them so that they do not come actually in contact, the percentage of voids will go up with decreasing size of the solids. As a matter of fact, we have seen that the voids in carbon black may run up to 95 percent or thereabouts. If the air-adsorption were negligible and if the particles were cubes of the same size and arranged in an orderly fashion the voids would be practically zero. As a matter of fact round-grained water-worn sands have 2–5 percent less voids than corresponding sharp grains of sand¹ because the former pack better. The difference between the theoretical values and the actual values as found under certain experimental conditions is shown by the statement that large enough masses of equal-sized marbles cannot be poured or tamped into a large vessel so as to give less than 44 percent voids. Undoubtedly these would have jarred down in time so as to occupy a lesser volume; because this result comes very close to that required for cubical piling. The effect of moisture on sand is also unexpected at first.² Moist sand occupies more space and weighs less per cubic foot than dry sand. The explanation of this apparent anomaly is that a film of water coats each grain of sand and separates it from the adjacent ones. Since fine sand has a large number of grains and consequently more surface area, addition

¹ TAYLOR and THOMPSON: Plain and Reinforced Concrete, 174 (1912).

² TAYLOR and THOMPSON: Plain and Reinforced Concrete, 176 (1912).

of water to it causes a greater increase in bulk than in the case of coarse sand. If a small quantity of water is poured into a vessel containing dry sand, the friction of the particles keeps the volume from increasing; but the bulk increases if the moistened sand is dumped out and then turned back into the vessel with a shovel or trowel. The percentage of water by weight which will give the greatest volume—corresponding to the largest percentage of voids—varies with different sands from 5 to 8 percent.

Since the densest mixture occurs with particles of different sizes, it is important, in making concrete, to grade the materials so as to get the maximum density.¹ On the other hand for a sand filter the grains of sand should be of approximately the same size,² as otherwise the filter clogs too readily. The question has also been raised but not answered, as to what are the proper sizes for the balls in the ball mill. Since there should probably be more of the small balls than the large ones, the proper ratio cannot be obtained if only large balls are added as the others wear down.³

A number of curious things in regard to wetted sand have been pointed out by Osborne Reynolds.⁴ If we have sand in maximum piling in a rubber bag and enough water to form a thin layer over the surface, squeezing the sand will necessarily cause it to expand or dilate, and the water will be sucked down into the dilated mass. We are familiar with this experiment in another form. The wet sand below high water mark is in the position of maximum piling. When one walks over this sand, the sand whitens momentarily and appears to dry around the foot. The sand is full of water, the surface of which is kept up to that of the sand by capillary attraction. The pressure of the foot dilates the sand and since the water does not suck up rapidly enough, the water level is lower in the dilated sand than before and consequently the sand appears dryer until more water has been brought up from below by capillary action. On raising the foot, the sand in and around the foot-print usually becomes wet momentarily, because the sand contracts when the shearing pressure is taken off and the excess of water is left momentarily on the surface.

¹ UPTON: *Materials of Construction*, 304 (1916).

² MENDELEEFF: *Jour. Chem. Soc.*, **48**, 114; LUEGER: *Ibid.* **48**, 198 (1885).

³ *Chem. Met. Eng.*, **14**, 285, 292 (1916)

⁴ *Phil. Mag.* (5) **20**, 469 (1885); *Scientific Papers*, **2**, 217 (1901).

In a filter press the solid to be filtered tends to go into cubical piling because that lets the water through most readily. If the crystals are displaced so that they pass into hexagonal piling, water will be set free. Hatschek¹ says in regard to this that it is a perfectly familiar fact that apparently dry cakes of calcium sulphate, for instance, which break with a clean fracture can be reduced to an almost liquid mass by mere shaking. It seems probable that in quicksands the sand is in a state of cubical piling, making it possible for a man to sink in it and raise the water without raising the sand.

To show some of the phenomena due to dilatancy Osborne Reynolds took a thin, transparent, india-rubber balloon, filled it with about six pints of sand and water, and closed it so that it contained no air. There was more than enough water to fill the voids when the sand was at maximum density but not enough to fill them when the sand was at minimum density. When this rubber sack was laid on the table, the elasticity of the rubber gave it a rounded shape. The sand settled into the condition of maximum piling and there was consequently a layer of water above the surface of the sand. The bag can be squeezed and altered in shape as though it had no firmness, so long as the sand does not rise to the surface of the water. If the bag is placed between two vertical boards and squeezed, it changes shape at first apparently without resistance, but soon comes to a dead stop. Turning it on its side and laying a 56 pound weight on it produced no further change in shape; but on removing the weight the bag goes back to its almost rounded shape. If the bag is shaken slightly while it is being squeezed, the sand keeps at its densest and the bag can be pressed out until it is a broad flat plate. The bag is soft so long as it is squeezed; but if the pressure is removed, the elasticity of the rubber tends to draw the bag back to its rounded form. This dilates the sand and causes the excess of water to be sucked into the pores. So soon as there is no excess of water, no further change takes place and the bag remains a flat cake with peculiar properties. It yields at once to pressure on its sides, such pressure having nothing but the elasticity of the bag to overcome because pressure in that direction causes the sand to contract. It is perfectly rigid,

¹ Jour. Soc. Chem. Ind., 21, 540 (1908).

however, to radial pressures because such pressures tend to dilate the sand still farther. When placed on its edge, it will hold up a hundred pounds. If, however, it is pressed sufficiently on the sides while holding up such a weight, all the strength vanishes and it is again a rounded bag of loose sand and water. By shaking the bag into a mould, it can be made to take any shape; then by drawing off the excess of water and closing the bag, the sand becomes perfectly rigid and will not change its shape unless the bag is torn. Since the sand is at its maximum density, no amount of shaking will produce a change. In this way bricks can be made of sand or fine shot with water in the thinnest india-rubber envelope and they will withstand as much pressure as an ordinary brick without change of shape.

The clay workers use the word plasticity in a special sense to denote that a clay is plastic and will burn to a coherent mass. From this point of view wet sand is not plastic because it falls to pieces when dried. To meet this definition we must have in the water some bonding material presumably in a gelatinous form. The film of water about the clay particles is usually assumed to be $50\mu\mu$ in thickness.¹ There is no difficulty in accounting for a gelatinous film.² Cushman³ has shown that the cementing power of rock powders is due to the formation of gelatinous silica, ferric, oxide, etc. If we have a gelatinous film which is adsorbed strongly by the solid particles and which can take up and lose water, we shall have plasticity. In the case of clay the gelatinous material may be hydrous alumina, hydrous silica, or some intermediate composition. The difficulty, however, is to account for its remaining plastic after moderate drying and for its readsorbing water to form a gelatinous mass. This is probably due to the presence of some salt; but we do not know what salt and consequently we cannot tell why one clay is plastic and another not, and we do not know what we should add to the non-plastic clay to make it plastic. People have never studied the problem from a rational point of view.

From this study of coalescence we conclude that liquid drops

¹ GROUT and POPPE: *Trans. Am. Ceramic Soc.*, **14**, 73 (1912); DAVIS: *Ibid.*, **16**, 19 (1914).

² QUINCKE: *Drude's Ann.*, **7**, 74 (1902).

³ *Jour. Am. Chem. Soc.*, **25**, 451 (1903).

or solid grains will coalesce or agglomerate if brought into actual contact. To keep them from doing so we must have a surface film of some sort. Since this coalescence or agglomeration takes place spontaneously, work must be done on the liquid or solid to disintegrate it. It is easy to see that a film might keep drops separated and yet not break up a large drop into a lot of smaller ones. Dirty mercury will remain indefinitely as a single liquid mass so far as we know. If we disintegrate the mass by shaking, a film will form over each drop and will keep the drops from coalescing. This "flouring" of mercury, as it is called, is a distinct source of trouble when extracting gold by the amalgamation process. In most cases the film is oxide, chloride, or grease, though it may consist of oxides of other metals if one starts with an amalgam. Anything that will dissolve the surface film will cause the drops of mercury to run together. Treatment with potassium cyanide is therefore very effective. Emulsions of oil in water are obtained if some substance like sodium oleate is present to form a film over the drops of oil, thus keeping them from coalescing.¹ It is easy to see that the work necessary to break up a liquid or solid mass into drops or grains will be less if we add something to the solution which will lower the surface tension of the liquid or solid. In some cases water alone will cause the disintegration. With gelatine we get reversible disintegration at very moderate temperatures, say 30°; but cellulose requires a very much higher temperature. We do not know at all to what extent this matter of disintegration depends upon the structure; but a single illustration from the field of true solutions will show the possibility of such a factor. If we place a crystal of rock candy in cold water the crystal dissolves so as to keep its shape approximately. It grows smaller but does not fall to pieces. If we put a lump of sugar into cold water, the smaller crystals which act as binding material dissolve first and the lump disintegrates to a mass of grains.

TYPES OF PRECIPITATES

Sufficiently finely divided particles will be kept in suspension in a liquid indefinitely by the Brownian movements, provided coalescence and the resulting agglomeration are prevented.

¹ Cf. DONNAN and PORTS: *Zeit. Kolloidchemie*, **7**, 208 (1910).

Such a colloidal solution is called a sol. One may use the words hydrosol, alcocol, etc., to show that the dispersing liquid is water, alcohol, etc. When the colloidal particles agglomerate and precipitate, the precipitate is called a gel, or a hydrogel in case the dispersing liquid is water. The word gel is also used to include a jelly, which differs from a gelatinous precipitate in that there is no supernatant liquid when first formed. It is really the general term for a solid or semi-solid colloid. The change from a gel to a sol is usually called peptization, a term which we owe to Graham. The reverse change from sol to gel was called pectization by Graham; but this term has never become popular. A stable colloidal solution will consist of very fine particles kept from agglomerating by a protecting film¹ of some sort, electrification being equivalent to a film.² Small particles³ may be obtained either by condensation from vapor or solution (usually called precipitation) or by disintegration of larger masses. The disintegration is often called peptization especially when done chemically, as opposed to mechanical or electrical disintegration. People have distinguished eight types of precipitates: crystalline; colloidal or non-settling; flocculent; curdy; sandy; gelatinous; jelly-like; fluid. A crystalline precipitate is one that is distinctly crystalline and settles rapidly, as when KOH is neutralized by H₂SO₄ or when moderately concentrated solutions of lead nitrate and potassium chromate are mixed. A non-settling precipitate may be anhydrous or hydrous; there is little or no agglomeration. A typical case is the precipitation of lead chromate from very dilute solutions of lead nitrate and potassium chromate.⁴ A flocculent precipitate is obtained when a non-settling, non-gelatinous precipitate agglomerates to a bulky mass. It is easy to obtain a flocculent precipitate of silver chloride from suitable solutions of silver nitrate and potassium chloride. Haber and Oordt⁵ call the precipitate of beryllium hydroxide flocculent; but I am not certain whether they are limiting the term sufficiently sharply. A curdy precipitate is obtained when a flocculent

¹ Cf. HÖBER: *Physikalische Chemie der Zelle und der Gewebe*, 233 (1914).

² Cf. HARDY: *Proc. Roy. Soc.*, **86A**, 601 (1912).

³ FREUNDLICH: *Kapillarchemie*, 527 (1909).

⁴ FREE: *Jour. Phys. Chem.*, **13**, 114 (1909).

⁵ *Zeit. anorg. Chem.*, **38**, 377 (1904).

precipitate agglomerates to a fairly dense mass. The typical case is, of course, the precipitation of caseine by acids, but a similar precipitate can be obtained with AgNO_3 and HCl . There is no sharp dividing line between a flocculent and a curdy precipitate. A sandy precipitate is obtained when a flocculent or a curdy precipitate agglomerates to a dense mass. The alumina from hot sodium aluminate in the Bayer process is a sandy precipitate.¹ A granular or sandy alumina is said to be precipitated by ammonia² at 66° . A gelatinous precipitate is always viscous; it involves agglomeration to a bulky form. Hydrous alumina and hydrous ferric oxide, when precipitated cold, are typical gelatinous precipitates. When a sparingly soluble salt is precipitated from very concentrated solutions we apparently always get a gelatinous precipitate. Thus gelatinous barium sulphate is obtained by mixing concentrated solutions of barium sulphocyanate and manganese sulphate,³ and gelatinous calcium carbonate by mixing concentrated solutions of calcium chloride and sodium carbonate. The difference between a gelatinous precipitate and a jelly is that the liquid phase is visible as such in the case of the gelatinous precipitate and is not in the case of the jelly. A jelly is always hydrous, viscous, and bulky; it may consist of a number of coalescing drops or rods, in which case both phases are continuous; or it may consist of coalescing films, in which case we have a honeycomb structure, with water as the internal phase. A typical jelly can be obtained with sodium silicate and hydrochloric acid. A fluid precipitate is one which is too mobile to be classed as a gelatinous precipitate. Sodium phenolate or sodium oleate with an excess of HCl gives a fluid precipitate.

The mean mass of the crystals in a crystalline precipitate is given by the total weight of the precipitate divided by the number of crystals. Experimentally we find that the number of nuclei increases less rapidly than the concentration at first and more rapidly later. When very dilute solutions are mixed, the number of nuclei is so large relatively to the weight of the precipitate that the particles themselves are very small. With increasing

¹ RUSS: *Zeit. anorg. Chem.*, **41**, 216 (1904).

² VON WEIMARN: *Gründzuge der Dispersoidchemie*, 67 (1911).

³ TAYLOR: *Chem. News*, **103**, 169 (1911).

concentration we get increasing size of crystals for a while and then decreasing size, because the number of nuclei then increases more rapidly than the concentration. At very high concentrations a gelatinous precipitate is always obtained, as has been pointed out. It is possible that we have here the appearance of a viscous and instable second liquid layer; but this has not yet been proved. According to Clowes a jelly is formed when a viscous phase separates slowly in presence of a substance which tends to keep it dispersed.¹ To obtain large crystals one must have a solution so slightly supersaturated that no nuclei form spontaneously and that no branched crystals form in presence of a single crystal.² Von Weimarn³ cites the case of a spring in which crystals of barium sulphate had grown 5 cm long! Geologists have prepared certain substances in distinct crystals by arranging for the slow diffusion of dilute solutions of two salts which form the desired substance by metathetical reaction. Johnston⁴ has improved on the technique by allowing the two solutions to diffuse into a large vessel containing water, causing a further dilution. Dreaper⁵ obtained distinct crystals by letting solutions diffuse through sand, the rate of diffusion being relatively slow on account of the capillary spaces. Holmes⁶ obtained crystals of silver bichromate in flat needles one cm long by this method, substituting aluminum powder for sand. He filled a small test-tube full of N/10 potassium iodide, covered the mouth of the tube with gold-beater's skin, and immersed the tube in a small beaker containing a saturated lead acetate solution. At once an almost amorphous precipitate of lead iodide appeared on the under side of the membrane and in less than a minute crystals of lead iodide fell in a gleaming shower to the bottom of the test-tube. If the same solutions are mixed in a

¹ Cf. HARDY: *Jour. Physiology*, **24**, 167 (1899), *Proc. Roy. Soc.*, **66**, 95 (1900); **87A**, 29 (1912); HOLMES and RINDFUSZ: *Jour. Am. Chem. Soc.*, **38**, 1970 (1916); HOLMES and FALL: *Ibid.*, **41**, 763 (1919).

² Cf. HOPKINS: *Am. Chem. Jour.*, **25**, 413 (1907); BOWMAN: *Jour. Soc. Chem. Ind.*, **25**, 143 (1906); HOSTETTER: *Jour. Washington Acad. Sci.*, **9**, 85 (1919); MOORE: *Jour. Am. Chem. Soc.*, **41**, 1060 (1919).

³ *Grundzüge der Dispersoidchemie*, 55 (1911).

⁴ *Jour. Am. Chem. Soc.*, **36**, 16 (1914).

⁵ *Jour. Soc. Chem. Ind.*, **32**, 678 (1913).

⁶ *Jour. Phys. Chem.*, **21**, 709 (1917).

test-tube without using a membrane, a yellow powder is obtained and no easily recognized crystals. This method as developed by Holmes seems the most promising of any because it appears to give results with more concentrated solutions and would presumably work even better with more dilute solutions. Excessive supersaturation and consequently the formation of very fine precipitates can be obtained by using a solvent in which the resulting salt is practically insoluble.¹ It is easier to avoid supersaturation when the substance is more soluble. Thus one can get crystals of silver chloride without trouble from an ammoniacal solution.² The effect of other substances in the solution depends on their effect on the supersaturation and whether they are adsorbed by the precipitate.

If a precipitate forms in the presence of a substance which is adsorbed strongly by it, the adsorption will prevent the growth of the crystals and the precipitate will therefore come down in a finer state of subdivision. A typical case is the precipitation of silver bromide in presence of gelatine. The addition agents in electrolytic refining are substances which move to the cathode under the influence of the current and which are adsorbed strongly by the metal as it comes out. Barium sulphate precipitates in a finely divided form in presence of barium chloride³ or potassium sulphate, both of which it adsorbs, and more coarsely crystalline in presence of sulphuric acid or hydrochloric acid.⁴ Barium sulphate shows selective adsorption for its own ions, which accounts for the behavior of barium chloride⁵ and potassium sulphate. The peptizing action of sulphate ions in sulphuric acid is cut down by the tendency of hydrogen ion to be adsorbed strongly. The precipitate is therefore more coarsely crystalline. The solvent action of hydrochloric acid is a factor in making the barium sulphate precipitate more coarsely crystalline.⁶ The question has been raised whether the finest precipitates are crystalline or amorphous. Von Weimarn⁷ calls them all crystal-

¹ BYK: *Zeit. Elektrochemie*, **13**, 38 (1907).

² REINDERS: *Zeit. phys. Chem.*, **77**, 696 (1911).

³ FOULK: *Jour. Am. Chem. Soc.*, **18**, 793 (1896).

⁴ MAR: *Jour. Chem. Soc.*, **60**, 1137 (1891).

⁵ WEISER: *Jour. Phys. Chem.*, **21**, 314 (1917).

⁶ See also OSBORNE: *Jour. Phys. Chem.*, **17**, 629 (1913).

⁷ *Zett. Kolloidchemie*, **3**, 166 (1908).

line; but he considers that liquids and gases are crystalline, which throws him out of court, because he is not using the word in the same sense as other people. A supercooled liquid like glass is amorphous in the ordinary sense of the term. Whether a precipitate is amorphous or not depends upon its being a supercooled liquid or not. Von Weimarn is undoubtedly right in saying that many precipitates are really crystalline, though they are classed as amorphous; but there is no question that there are amorphous precipitates.

In many cases there is a gradual change from an amorphous precipitate to a crystalline one on standing¹ and still more on heating.² At higher temperatures precipitates are less hydrous and tend to be more coarsely crystalline. There are no data in regard to a substance like sodium sulphate which is less soluble at 80° than at 40°. When barium sulphate is precipitated hot it does not run through the filter so readily as when precipitated cold. Other conditions being the same, a non-settling silver³ is obtained by reduction with hydrazine at 16° and pulverulent silver by reduction at 80° to 90°.

THEORY OF PEPTIZATION

We find experimentally that certain solutions will peptize or disintegrate certain precipitates so that we get colloidal solutions. This is always the result of adsorption. Theoretically there are three possibilities. If an adsorbed film has a low surface tension on the water side and a high one on the other side, it will tend to scrunch up and to peptize the solid as internal phase. If the reverse is the case, the solid will tend to form the external phase. If the two surface tensions are practically equal, neither will prevail. Some adsorbed substances seem to have practically no peptizing action;⁴ but these cases should be studied again in the light of what we now know about colloid chemistry. Tenta-

¹ WATSON: Jour. Chem. Soc., **60**, 875 (1891); GILBERT: Jour. Phys. Chem., **18**, 86 (1914).

² MOURET: Comptes rendus, **123**, 54 (1896); DOELTER: Zeit. Kolloidchemie, **7**, 29, 86 (1910); GALPIN: Trans. Am. Ceramic Soc., **14**, 337 (1912).

³ GUTBIER: Zeit. Kolloidchemie, **4**, 308 (1909).

⁴ DOYLE: Jour. Phys. Chem., **17**, 390 (1913).

...tive theories of peptization have been discussed by Lottermoser,¹ Jordis,² Mecklenburg,³ and von Weimarn.⁴ If we adopt Freundlich's view that adsorption always lowers the surface tension, a theory of peptization follows at once. We may have peptization by a liquid, by a non-electrolyte, by an adsorbed ion, by a salt, or by a peptized colloid. When a liquid is adsorbed by a solid, it will tend to peptize it and in some cases will do so. Water peptizes tannin, amyl acetate peptizes pyroxylin, and fused baths peptize metals. At higher temperatures the peptizing action increases, and we may get glass peptized by water⁵ or vulcanized rubber by various organic liquids.⁶ If the amount of substance peptized by a given mass of water under given conditions is fairly constant, it will look as though we were dealing with true solubility. In fact, data are to be found in the literature for the solubility of tannin in water.

There are a number of cases where mixed solvents will peptize a solid much better than either one alone—cellulose nitrates in ether and alcohol, caseine in pyridine and water,⁷ and probably cinchonine in chloroform and alcohol,⁸ as well as phloretine in ether and water.⁹ The theory of this has not been worked out. Cellulose nitrate swells in alcohol and not in ether;¹⁰ but it is not known whether this is universal. We do not know whether alcohol peptizes cellulose nitrate at higher temperatures. Zein is also peptized in mixed solvents.¹¹ Larguier des Bancels¹² claims that gelatine is peptized more readily by aqueous alcohol or aqueous acetone than by water alone.

¹ Jour. prakt. Chem. (2) **68**, 341 (1903); **72**, 39 (1905); **73**, 374 (1906); Zeit. phys. Chem., **62**, 371 (1908).

² Van Bemmelen Gedenkboek, 215 (1910).

³ Zeit. anorg. Chem., **74**, 260 (1912).

⁴ Lehre von den Zuständen der Materie, **1**, 160 (1914)

⁵ BARUS: Am. Jour. Sci. (3) **38**, 408 (1869); **41**, 110 (1891); (4) **6**, 270 (1898); **7**, 1 (1899); Phil. Mag. (5) **47**, 104, 461 (1899).

⁶ BARUS: Am. Jour. Sci. (3) **42**, 359 (1891).

⁷ LEVITES: Zeit. Kolloidchemie, **8**, 4 (1911).

⁸ OUDEMANN: Jour. Chem. Soc., **26**, 533 (1873).

⁹ SCHIFF: Zeit. phys. Chem., **23**, 355 (1897).

¹⁰ Private communication from Professor Chamot.

¹¹ GALEOTTI and GIAMPALMO: Zeit. Kolloidchemie, **3**, 118 (1908).

¹² Comptes rendus, **146**, 290 (1911).

Relatively little work has been done on direct peptization by means of a dissolved non-electrolyte, but a good deal of stress has been laid on the cases where a non-electrolyte prevents the formation of a visible precipitate. A concentrated solution of sugar in water will prevent the precipitation of calcium silicate,¹ silver chromate, and silver chloride;² also of lime and of the hydrous oxides of copper³ uranium, and iron.⁴ Invert sugar is about seven times as effective as cane sugar in holding up hydrous ferric oxide. Grimaux⁵ showed that glycerine prevents the precipitation of hydrous ferric oxide by caustic potash.

If one ion of an electrolyte is adsorbed more than the other ion, it will tend to peptize the adsorbing material and to give rise to a colloidal solution containing positively or negatively charged particles according to the nature of the adsorbed ion. Freshly precipitated silver halides are peptized by dilute silver nitrate or the corresponding potassium halide,⁶ the silver and the halide ions being adsorbed strongly. Many oxides are peptized by their chlorides or nitrates, forming so-called basic salts.⁷ Sulphides are peptized by hydrogen sulphide.⁸ Gelatine is liquefied or peptized by a potassium iodide solution. The peptization of hydrous oxides by caustic alkali can be considered as a case of common ion or as the preferential adsorption of hydroxyl ion. Hydrous chromic oxide gives an apparently clear green solution when treated with an excess of caustic potash; but the green oxide can be filtered out completely by means of a collodion

¹ WEISBERG: Bull. Soc. chim., Paris, (3) **15**, 1097 (1896).

² LOBRY DE BRUYN: Ber. deutsch. chem. Ges., **35**, 3079 (1902).

³ GRAHAM: Jour. Chem. Soc., **15**, 253 (1862).

⁴ RIFFARD: Comptes rendus, **77**, 1103 (1873).

⁵ Comptes rendus, **98**, 1485, 1540 (1884).

⁶ LOTTERMOSER: Jour. prakt. Chem. (2) **60**, 341 (1903); **72**, 39 (1905); **73**, 374 (1906); Zeit. phys. Chem., **62**, 371 (1908).

⁷ GRAHAM: Jour. Chem. Soc., **15**, 254 (1862); MÜLLER: Ber. deutsch. chem. Ges., **39**, 2856 (1906); Zeit. anorg. Chem., **52**, 316 (1907); SZILARD: Jour. Chim. phys., **5**, 488, 636 (1907).

⁸ SPRING: Ber. deutsch. chem. Ges., **16**, 1142 (1883); PROST: Jour. Chem. Soc., **54**, 653 (1888); WINSSINGER: Bull. Soc. chim., Paris (3) **49**, 452 (1888); LINDER and PICTON: Jour. Chem. Soc., **61**, 116 (1892); MEUNIER: Comptes rendus, **124**, 1151 (1897); YOUNG: Jour. Phys. Chem., **21**, 141 (1917).

filter, a colorless solution passing through.¹ Hantzsch² considers that hydrous beryllium oxide is peptized by caustic alkali³ and so is cobalt oxide.⁴ In ammoniacal copper solutions part of the copper oxide is apparently colloidal and part dissolved.⁵ Freshly precipitated zinc hydroxide is peptized by alkali; but the solution is very unstable, the zinc hydroxide often coagulating inside half an hour. The relatively small amount of zinc remaining in solution is present chiefly or entirely as sodium zincate.⁶ The bulk of the evidence seems to be that alumina is not peptized appreciably by alkali and that it goes into solution as sodium aluminate,⁷ though the other view has been supported.⁸ Adsorption of hydroxyl ion accounts for the peptization of silicic acid⁹ and of caseine by alkalies. Caseine can also be peptized by acids. A. Müller¹⁰ has prepared colloidal solutions of aluminum, iron, cobalt, thorium, and yttrium oxides by peptization with dilute hydrochloric acid, and Bentley and Rose¹¹ have peptized freshly precipitated alumina with 8 percent acetic acid. It is possible but not probable, that the peptization is done by a trace of metallic salt formed by the acid and not by the hydrogen ion.

There are no cases where it has been shown conclusively that

¹ FISCHER and HERZ: *Zeit. anorg. Chem.*, **31**, 352 (1902); FISCHER: *Ibid.*, **40**, 39 (1904); NAGEL: *Jour. Phys. Chem.*, **19**, 331, 569 (1915).

² *Zeit. anorg. Chem.*, **30**, 289 (1902).

³ LOEW: *Zeit. anal. Chem.*, **8**, 463 (1870); FISCHER: *Zeit. anorg. Chem.*, **40**, 39 (1904).

⁴ TUBANDT: *Zeit. anorg. Chem.*, **45**, 368 (1905).

⁵ PÉLIGOT: *Ann. Chim. Phys.* (3) **63**, 343 (1861); GUIGNET: *Comptes rendus*, **55**, 741 (1862); GRIMAUD: *Ibid.*, **89**, 1434 (1884).

⁶ HANTZSCH: *Zeit. anorg. Chem.*, **30**, 289 (1902); **75**, 371 (1912); FISCHER and HERZ: *Zeit. anorg. Chem.*, **31**, 352 (1902); KLEIN: *Zeit. anorg. Chem.*, **74**, 157 (1912).

⁷ HERZ: *Zeit. anorg. Chem.*, **25**, 155 (1900); HANTZSCH: *Zeit. anorg. Chem.*, **30**, 289 (1902); RUBENBAUER: *Zeit. anorg. Chem.*, **30**, 331 (1902); SLADE: *Jour. Chem. Soc.*, **93**, 421 (1908); *Zeit. anorg. Chem.*, **77**, 457 (1912); *Trans. Faraday Soc.*, **10**, 150 (1914); BLUM: *Jour. Am. Chem. Soc.*, **35**, 1499 (1913).

⁸ MAHIN, INGRAHAM AND STEWART: *Jour. Am. Chem. Soc.*, **35**, 30 (1913).

⁹ GRAHAM: *Jour. Chem. Soc.*, **17**, 324 (1864).

¹⁰ SVEDBERG: *Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe*, 400 (1909).

¹¹ *Jour. Am. Chem. Soc.*, **35**, 1490 (1913).

peptization is due chiefly to adsorption of undissociated salt,¹ but undoubtedly such instances will be found. Water-peptizable colloids like gelatine,² gum arabic,³ dextrine,⁴ soap,⁵ or saponin⁶ will peptize many precipitates and they are often called protecting colloids because they prevent the agglomeration and consequent settling of finely divided precipitates. Caseine is not peptized by water; but acts as a protecting colloid when peptized by acids or alkalis. Hydrous chromic oxide when peptized by caustic potash, can then prevent the precipitation of hydrous ferric oxide, etc. If too much ferric oxide is present, all the chromic oxide is carried down by it.⁷ Solutions of copper oxide in ammonia will peptize chromic oxide.⁸ Molybdic acid is not precipitated from its salts by uranyl salts, but tungstic acid is. In presence of tungstic acid, practically all the molybdic acid is precipitated. This is obviously a case of adsorption and the converse is also true that no tungstic acid would be precipitated in presence of a sufficient excess of a molybdate.⁹ Aniline dyes, which are insoluble in benzene can be peptized by a benzene-soluble colloid such as the so-called zinc or magnesium resinate.¹⁰

Since a colloidal solution is one in which a finely divided phase is kept from coalescing in some way, it is clear that there may be any number of colloidal aluminas, for instance, varying from anhydrous alumina (Al_2O_3) up to the most highly hydrous form that can be obtained. As a matter of fact, people have generally been satisfied with distinguishing only two sets of colloidal solutions, which they have called solutions of alumina and meta-

¹ It seems probable that the peptization of caseine by acetic acid is due largely to the undissociated acid.

² Eder's *Handbuch der Photographie*, 5th Ed., 3 I, 28 (1902); LÜPPO-CRAMER: *Phot. Correspondenz*, 44, 578 (1907).

³ LEFORT and THIBAUT: *Jour. Chem. Soc.*, 42, 1322 (1882).

⁴ LACHAUD: *Bull. Soc. chim.*, Paris (3) 15, 1105 (1896).

⁵ SPRING: *Zeit. Kolloidchemie*, 4, 161 (1909); 6, 11, 109, 164 (1910).

⁶ SCHIAPARELLI: *Jour. Chem. Soc.*, 46, 333 (1884).

⁷ NORTHCOTE and CHURCH: *Jour. Chem. Soc.*, 6, 54 (1854); NAGEL: *Jour. Phys. Chem.*, 19, 331 (1915).

⁸ PRUDHOMME: *Jour. Chem. Soc.*, 25, 672 (1872).

⁹ MISS HITCHCOCK: *Jour. Am. Chem. Soc.*, 17, 483, 520 (1895); WÖHLER: *Zeit. Elektrochemie*, 16, 693 (1910); WÖHLER and ENGELS: *Kolloidchemische Beihefte*, 1, 454 (1910).

¹⁰ SOXHLET: *Art of Dyeing and Staining Marble, etc.*, 76 (1902).

~~ter~~mina, of stannic and metastannic acids, etc.¹ While adsorption will cause peptization under suitable conditions, the disintegrating power of the adsorbed substance is relatively small and often will not be sufficient to break up solid masses. A protecting colloid, for instance, will prevent the formation of a precipitate when it may not be able to disintegrate a massive precipitate.

¹ HANTZSCH: Zeit. anorg. Chem., **30**, 338 (1902).